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(54) **Herbizide Mittel auf Basis von Piperidin-Derivaten**

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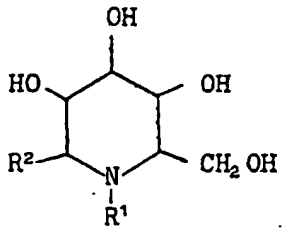
Patentansprüche

1) Herbizide Mittel, gekennzeichnet durch einen Gehalt an mindestens einem 2-Hydroxymethyl-3,4,5-trihydroxy-piperidin-Derivat der allgemeinen Formel



(I)

in welcher

$R^1$ für Alkyl mit mehr als 4 Kohlenstoffatomen, Alkenyl, Alkadienyl, Alkinyl, Hydroxyalkyl und die Gruppierung $-X-R^3$ steht, wobei

X für Alkylen oder Alkenylen steht und

$R^3$ für gegebenenfalls substituiertes Aryl, gegebenenfalls substituiertes Aryloxy, gegebenenfalls substituiertes Arylmercapto, gegebenenfalls substituiertes Pyridyl, Alkoxy, Alkoxyalkoxy, Alkylthio, Amino, Hydroxycarbonyl, gegebenenfalls sbustituiertes Cycloalkyl und gegebenenfalls substituiertes Cycloalkenyl steht,

$R^1$ auch für Wasserstoff oder Alkyl mit 1 bis 4 Kohlenstoffatomen steht, wenn $R^2$ für einen anderen Rest als Wasserstoff steht,

$R^2$ für Wasserstoff, Cyano, Hydroxy, Hydroxymethyl, Hydroxysulfonyl, Aminomethyl, Alkylaminomethyl, Hydroxycarbonyl, Alkoxycarbonyl sowie die Gruppierungen $-CO-NH-R^4$, $-CH_2-NH-CO-R^5$, $-CH_2-NH-SO_2-R^5$, $-CH_2-NH-CO(S)-NH-R^5$ und $-CH_2-NH-CO-OR^5$ steht, wobei

$R^4$ für Wasserstoff, Alkyl oder gegebenenfalls substituiertes Aralkyl steht und

$R^5$ für Alkyl, gegebenenfalls substituiertes Aryl, gegebenenfalls substituiertes Aralkyl, Cyanalkyl, Aminoalkyl oder Halogenalkyl steht.

2) Verfahren zur Bekämpfung von Unkräutern, dadurch gekennzeichnet, daß man 2-Hydroxymethyl-3,4,5-trihydroxy-piperidin-Derivate gemäß Formel (I) in Anspruch 1 auf die Unkräuter oder ihren Lebensraum einwirken läßt.

3) Verwendung von 2-Hydroxymethyl-3,4,5-trihydroxy-piperidin-Derivaten gemäß Formel (I) in Anspruch 1 zur Bekämpfung von Unkraut.

4) Verfahren zur Herstellung von herbiziden Mitteln, dadurch gekennzeichnet, daß man 2-Hydromethyl-3,4,5-trihydroxy-piperidin-Derivate gemäß Formel (I) in Anspruch 1 mit Streckmitteln und/oder oberflächenaktiven Mitteln vermischt.

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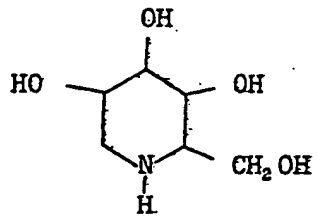
# Herbizide Mittel auf Basis von Piperidin-Derivaten

Die vorliegende Erfindung betrifft die Verwendung von weitgehend bekannten 1- und/oder 6-substituierten 2-Hydroxymethyl-3,4,5-trihydroxy-piperidin-Derivaten (=N- und/oder 1-substituierten 1-Desoxy-nojirimycin-Derivaten) als Herbizide.

Es ist bereits bekannt geworden, daß das pharmakologisch wirksame 2-Hydroxymethyl-3,4,5-trihydroxy-piperidin (=1-Desoxy-nojirimycin) der Formel




(A)

(vgl. DE-OS 26 56 602) auch eine herbizide Wirkung aufweist (vgl. Veröff. JP-Patentanmeldung Nr. 55-7224). Das 1-Desoxy-nojirimycin ist jedoch nur ein verhältnismäßig schwaches Herbizid, das insbesondere gegen bestimmte wichtige Unkräuter keine befriedigende Wirkung zeigt.

Es ist außerdem bekannt, daß bestimmte weitere 3,4,5-Trihydroxy-piperidin-Derivate als Arzneimittel verwendet werden können (vgl. DE-OS 27 58 025; veröff. EP-Patentanmeldung Nr. 0 000 947). Eine herbizide Wirksamkeit dieser Verbindungen ist jedoch nicht beschrieben.



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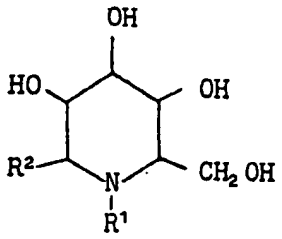
Es wurde nun gefunden, daß die 2-Hydroxymethyl- 3,4,5-trihydroxy-piperdin-Derivate der allgemeinen Formel



(I)

in welcher

$R^1$ für Alkyl mit mehr als 4 Kohlenstoffatomen, Alkenyl, Alkadienyl, Alkinyl, Hydroxyalkyl und die Gruppierung $-X-R^3$ steht, wobei

X für Alkylen oder Alkenylen steht und

$R^3$ für gegebenenfalls substituiertes Aryl, gegebenenfalls substituiertes Aryloxy, gegebenenfalls substituiertes Arylmercapto, gegebenenfalls substituiertes Pyridyl, Alkoxy, Alkoxyalkoxy, Alkylthio, Amino, Hydroxycarbonyl, gegebenenfalls substituiertes Cycloalkyl und gegebenenfalls substituiertes Cycloalkenyl steht,

$R^1$ auch für Wasserstoff oder Alkyl mit 1 bis 4 Kohlenstoffatomen steht, wenn $R^2$ für einen anderen Rest als Wasserstoff steht,

$R^2$ für Wasserstoff, Cyano, Hydroxy, Hydroxymethyl, Hydroxysulfonyl, Aminomethyl, Alkylaminomethyl, Hydroxycarbonyl, Alkoxycarbonyl sowie die Gruppierungen $-CO-NH-R^4$, $-CH_2-NH-CO-R^5$, $-CH_2-NH-SO_2-R^5$, $-CH_2-NH-CO(S)-NH-R^5$ und $-CH_2-NH-CO-OR^5$ steht, wobei

$R^4$ für Wasserstoff, Alkyl oder gegebenenfalls substituiertes Aralkyl steht, und

$R^5$ für Alkyl, gegebenenfalls substituiertes Aryl, gegebenenfalls substituiertes Aralkyl, Cyanalkyl, Aminoalkyl oder Halogenalkyl steht,

gute herbizide Eigenschaften aufweisen.

Die Verbindungen der Formel (I) können gegebenenfalls als geometrische und/oder optische Isomeren vorliegen. Die vorliegende Erfindung umfaßt sowohl die einzelnen Isomeren als auch die Isomerengemische.

Überraschenderweise zeigen die erfindungsgemäß verwendbaren 2-Hydroxymethyl-3,4,5-trihydroxy-piperidin-Derivate der Formel (I) eine erheblich höhere herbizide Wirkung als das aus dem Stand der Technik bekannte 1-Desoxy-nojirimycin, welches chemisch und wirkungsmäßig die nächstliegende Verbindung ist. Die erfindungsgemäße Verwendung der Stoffe der Formel (I) stellt somit eine Bereicherung der Technik dar.

Die erfindungsgemäß verwendbaren 2-Hydroxymethyl-3,4,5-trihydroxy-piperidin-Derivate sind durch die Formel (I) allgemein definiert. In dieser Formel steht $R^1$ vorzugsweise für geradkettiges oder verzweigtes Alkyl mit 5 bis 18 Kohlenstoffatomen, Alkenyl mit 2 bis 12 Kohlenstoffatomen, Alkadienyl mit 4 bis 8 Kohlenstoffatomen, Alkinyl mit 2 bis 6 Kohlenstoffatomen, Hydroxyalkyl mit 1 bis 6 Kohlenstoffatomen und 1 bis 3 Hydroxygruppen, sowie für die Gruppierung $-X-R^3$. $R^1$ steht außerdem auch vorzugsweise für Wasserstoff oder Alkyl mit 1 bis 4 Kohlenstoffatomen, wenn $R^2$ für einen anderen Rest als Wasserstoff steht.

X steht vorzugsweise für eine geradkettige oder verzweigte Alkylenkette mit 1 bis 12 Kohlenstoffatomen oder eine geradkettige oder verzweigte Alkenylenkette mit 2 bis 12 Kohlenstoffatomen.

$R^3$ steht vorzugsweise für gegebenenfalls substituiertes Aryl, Aryloxy und Arylmercapto mit jeweils 6 bis 10 Kohlenstoffatomen, wobei als Substituenten vorzugsweise genannt seien: Halogen, Alkyl mit 1 bis 4 Kohlenstoffatomen, Halogenalkyl mit 1 bis 2 Kohlenstoff- und 1 bis 5 gleichen oder verschiedenen Halogenatomen, Alkoxy, Alkylthio und Alkylsulfonyl mit je 1 bis 4 Kohlenstoffatomen, Hydroxy, Cyano, Nitro, Amino, Alkylamino, Dialkylamino und Alkylcarbonylamino mit jeweils 1 bis 2 Kohlenstoffatomen je Alkylrest, Hydroxycarbonyl (-COOH), Alkoxycarbonyl mit 1 bis 4 Kohlenstoffatomen im Alkylrest, sowie gegebenenfalls durch Halogen substituiertes Phenyl, Phenoxy und Benzyl.

$R^3$ steht weiterhin vorzugsweise für gegebenenfalls durch Halogen und Alkyl mit 1 bis 2 Kohlenstoffatomen substituiertes Pyridyl, für Alkoxy, Alkoxy-alkoxy und Alkylthio mit 1 bis 4 Kohlenstoffatomen je Alkylteil, Amino, Hydroxycarbonyl, Alkoxycarbonyl mit 1 bis 4 Kohlenstoffatomen im Alkylteil, sowie für gegebenenfalls durch Alkyl mit 1 bis 4 Kohlenstoffatomen substituiertes Cycloalkyl und Cycloalkenyl mit jeweils 5 bis 7 Kohlenstoffatomen.

$R^2$ steht vorzugsweise für Wasserstoff, Cyano, Hydroxy, Hydroxymethyl, Hydroxysulfonyl, Hydroxycarbonyl, Aminomethyl, Alkylaminomethyl mit 1 bis 4 Kohlenstoffatomen im Alkylteil, Alkoxycarbonyl mit 1 bis 4 Kohlenstoffatomen, sowie die Gruppierungen $-CO-NH-R^4$, $-CH_2-NH-CO-R^5$, $-CH_2-NH-SO_2-R^5$, $-CH_2-NH-CO(S)-NH-R^5$ und $-CH_2-NH-CO-OR^5$.

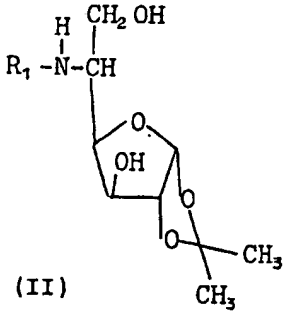
$R^4$ steht vorzugsweise für Wasserstoff, Alkyl mit 1 bis 4 Kohlenstoffatomen, sowie für gegebenenfalls substituiertes Aralkyl mit 6 bis 10 Kohlenstoffatomen im Arylteil und 1 bis 4 Kohlenstoffatomen im Alkylteil, wobei als Arylsubstituenten vorzugsweise die bereits oben bei der Definition des Restes $R^3$ genannten Substituenten infrage kommen.

$R^5$ steht vorzugsweise für Alkyl mit 1 bis 12 Kohlenstoffatomen, Cyanalkyl und Aminoalkyl mit 1 bis 12 Kohlenstoffatomen je Alkylteil, Halogenalkyl mit 1 bis 4 Kohlenstoff- und 1 bis 5 gleichen oder verschiedenen Halogenatomen, sowie für gegebenenfalls substituiertes Aryl und Aralkyl mit jeweils 6 bis 10 Kohlenstoffatomen im Arylteil und 1 bis 4 Kohlenstoffatomen im

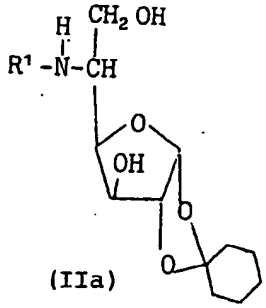
Alkylteil, wobei als Substituenten vorzugsweise die bereits oben bei der Definition des Restes $R^3$ genannten Substituenten infrage kommen.

Unter Halogen ist vorzugsweise jeweils Chlor und Fluor zu verstehen.

Die erfindungsgemäß zu verwendenden Wirkstoffe sind teilweise bekannt (vgl. EP 0 000 947), teilweise sind sie Gegenstand von eigenen älteren Patentanmeldungen (vgl. die deutschen Patentanmeldungen P 29 25 943.6 und P 30 07 078.1). Die Verbindungen der Formel (I) können nach den dort angegebenen Verfahren hergestellt werden. So werden Verbindungen der Formel (I) mit $R^2$=OH erhalten, indem man in Verbindungen der Formeln (II) oder (IIa)



(II)



(IIa)

in denen $R^1$ die oben angegebene Bedeutung hat,

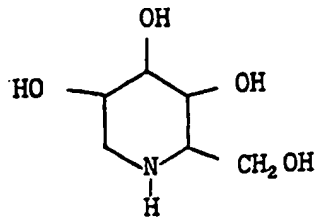
durch vorsichtige Säurehydrolyse die Isopropyliden- oder Cyclohexylidenschutzgruppen entfernt, wobei es gegebenenfalls zweckmäßig ist, die durch Ringerweiterung gebildeten Verbindungen der Formel (I) mit $R^2$ = OH in der Form von Addukten der schwefligen Säure oder der Blausäure abzufangen ($R^2$ = $-OSO_2H$ oder

CN). Aus den Bisulfitadditionsprodukten (d.h. sauren Schwefligsäureestern) werden die Verbindungen der Formel (I) mit $R^2$ = OH durch Behandlung mit Basen, vorzugsweise Erdalkalihydroxiden wie $Ca(OH)_2$ oder $Sr(OH)_2$, insbesondere aber $Ba(OH)_2$, in Freiheit gesetzt. Durch Umsetzung mit Wasserstoff-Donor-Reduktionsmitteln, wie beispielsweise $NaBH_4$, werden aus den Verbindungen der Formeln (I) mit $R^2$=OH die Verbindungen der Formel (I) mit $R^2$=H gewonnen.

Bestimmte Verbindungen der Formel (I) können auch erhalten werden, wenn man die Verbindungen der Formel (I) mit $R^2$=OH in an sich bekannter Weise mit Blausäure zu Verbindungen der Formel (I) mit $R^2$=CN umsetzt und gegebenenfalls aus diesen durch katalytische Hydrierung der Nitrilgruppe Verbindungen mit $R^2$= $-CH_2NH_2$ herstellt, und die Aminogruppe gegebenenfalls in an sich bekannter Weise zu Verbindungen, bei denen $R^2$= $-CH_2-NH-CO-R^5$ oder Alkylamino ist, acyliert, sulfonyliert, alkyliert, bzw. mit Chlorkohlensäureestern, Isocyanaten oder Senfölen derivatisiert.

Die Verbindungen der Formel (I), bei denen $R^2$= -COOH ist, werden erhalten, indem man Verbindungen der Formel (I) mit $R^2$= -CN in an sich bekannter Weise hydrolysiert. Aus den so erhaltenen Carbonsäuren lassen sich in an sich bekannter Weise Verbindungen der Formel (I) mit $R^2$= -COOAlkyl durch Umsetzung mit entsprechenden Alkoholen, Verbindungen der Formel (I) mit $R^2$= $-CONHR^4$ durch Aminolyse der Ester mit Aminen der allgemeinen Formel $R^4-NH_2$ erhalten.

N-substituierte Verbindungen der Formel (I) mit $R^2$=H werden auch erhalten, wenn man die Verbindung der Formel (III), d.h. 1-Desoxy-nojirimycin,



(III) = (A)

entweder mit Aldehyden der Formel

$$O = CH - R^1 \qquad (IV)$$

in welcher

$R^1$ die oben angegebene Bedeutung hat,

in Gegenwart eines Wasserstoff-Donor-Reduktionsmittels umsetzt, oder

mit reaktiven Alkylierungsmitteln der Formel

$$Z - R^1 \qquad (V)$$

in welcher

$R^1$ die oben angegebene Bedeutung hat und

Z für Halogen oder die $-OSO_3$-Gruppe steht,

in üblicher Weise umsetzt. Anstelle der Verbindungen

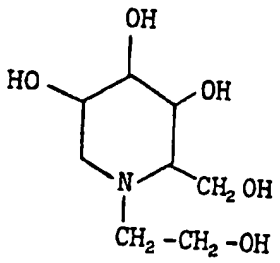
der Formel (V) können auch andere reaktive Alkylierungsmittel, wie z.B. Ethylenoxid, verwendet werden.

Weitere Einzelheiten zu den verschiedenen Verfahrensweisen können der Veröff. EP-Patentanmeldung Nr. 0 000 947 sowie den nachfolgenden Herstellungsbeispielen entnommen werden.

Die Ausgangsprodukte der Formeln (II), (IIa), (III), (IV) und (V) sind allgemein bekannte Verbindungen der organischen Chemie, bzw. sind sie und ihre Herstellung in der EP-Patentanmeldung Nr. 0 000 947 beschrieben.

Herstellungsbeispiele:

Beispiel 1

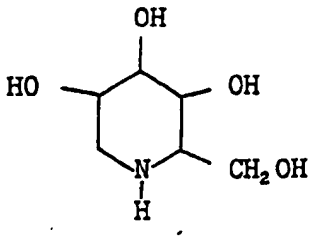


(1)

90,0 g 1-Desoxynojirimycin (A) wurden in 450 ml $H_2O$ gelöst und bei 5°C mit $CO_2$ gesättigt. Die Mischung wurde 20 Stunden bei 20°C gerührt, dann auf 5°C gekühlt und nochmals mit $CO_2$ gesättigt. 27,97 g Ethylenoxid wurden flüssig abgewogen und in einem Guß hinzugefügt. Das Reaktionsgemisch wurde 30 Minuten bei 5°C bis 10°C gerührt, dann innerhalb von 30 Minuten auf 50°C erhitzt und 6 Stunden bei 50 °C gerührt. Nach weiterem 20-stündigem Rühren bei 20°C wurde aufgearbeitet. Das Reaktionsgemisch wurde am Rotationsverdampfer eingeengt, der Rückstand wurde mit 2-Methoxyethanol zum Sieden erhitzt und mit Aktivkohle geklärt. Man ließ das Produkt bei 20°C auskristallisieren. Es wurde abgesaugt, mit 2-Methoxyethanol, dann mit Ethanol nachgewaschen und getrocknet. Die so erhaltenen 84,2 g N-(ß-Hydroxyethyl)-1-desoxynojirimycin mit einem Schmelzpunkt von 144-145,5°C wurden aus 90%igem Ethanol umkristallisiert. Ausbeute an N-(ß-Hydroxyethyl)-1-desoxynojirimycin (1): 78,3 g mit einem Schmelzpunkt von 147-149°C.

Die Verbindung (1) kann auch als 1-(ß-Hydroxyethyl)-2-hydroxymethyl-3,4,5-trihydroxy-piperidin bezeichnet werden.

Herstellung des Ausgangsproduktes

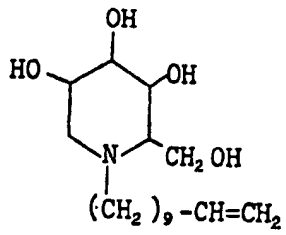


(A)

Eine Lösung von 2 g 5-Amino-5-desoxy-1,2-isopropyliden-α-D-glucofuranose in 8 ml 2 n Salzsäure wird 24 Stunden gerührt. Es wird mit 5 ml Wasser verdünnt und nach Zugabe von 0,69 g Triethylamin und 0,3 g Raney-Nickel 5 Stunden bei 3,5 bar hydriert. Es wird vom Katalysator abfiltriert, im Vakuum eingeengt und noch zweimal jeweils nach Zusatz von wenig Ethanol eingeengt, wobei Kristallisation eintritt. Die Kristalle werden mit Ethanol verrührt, abgesaugt und gut mit Ethanol gewaschen. Man erhält 1,45 g (79,7 % der Theorie) 1-Desoxy-nojirimycinhydrochlorid (A) vom Schmelzpunkt 209-210°C unter Zersetzung.

Aus dem Hydrochlorid wird in üblicher Weise die freie Base erhalten.

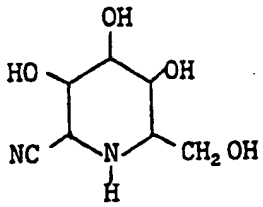
Beispiel 2



(2)

Zu 7,4 g 1-Desoxynojirimycin in 150 ml Methanol und 6,7 ml Eisessig gibt man 17 ml 10-Undecenol und 3 g Natriumcyanborhydrid ($NaCNBH_3$). Man rührt 2 Stunden bei Raumtemperatur. Anschließend wird das Reaktionsgemisch auf eine mit stark saurem Ionenaustauscher ($H^{\oplus}$-Form) gefüllte Säule aufgetragen. Es wird zuerst mit Methanol/Wasser=2:1, anschließend mit Ethanol / 6%-igem Ammoniak=2:1 eliminiert. Das ammoniakalische Eluat wird eingeengt. Der Rückstand wird aus Wasser kristallisiert. Ausbeute: 11,7 g N-Undecen-10-yl-1-dexoxy-nojirimycin (2) vom Schmelzpunkt 144-146°C.

Beispiel 3



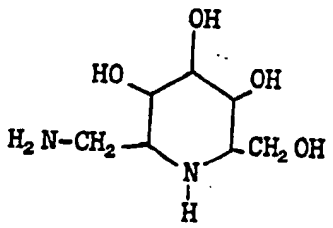
(3)

Zu 200 ml Wasser und 21,2 g $Ba(OH)_2 \times H_2O$ gibt man 17,5 g Nojirimycinbisulfitaddukt. Man rührt eine Stunde bei Raumtemperatur und saugt den Feststoff ab. Das Filtrat versetzt man mit 12 ml flüssiger Blausäure und läßt 1/2 Stunde rühren. Die Lösung wird erneut

filtriert und am Rotationsverdampfer bis auf 20 ml eingeengt. Man versetzt zunächst mit 20 ml Methanol, wobei das gewünschte Produkt auszukristallisieren beginnt, und vervollständigt die Kristallisation durch Zugabe von 100 ml Ethanol. Der Niederschlag wird abgesaugt.

Ausbeute : 12,0 g 1-Cyano-1-desoxynojirimycin (3) vom Schmelzpunkt 152-153°C. Nach Umkristallisation aus Methanol und wenig Wasser schmilzt die Substanz bei 155-156°C.

Beispiel 4

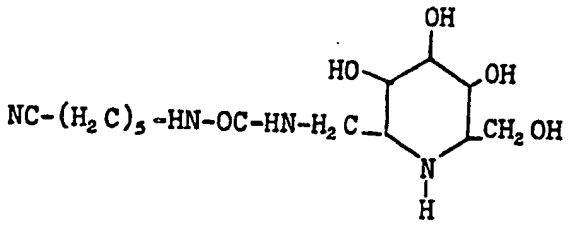



(4)

5 g 1-Cyano-1-desoxynojirimycin (Beispiel 3) werden in 100 ml Wasser mit 10 g Raney-Nickel als Katalysator eine Stunde bei 3,5 Atmosphären $H_2$-Druck in einer Schüttelbirne hydriert. Dann wird vom Katalysator abgesaugt und die Lösung wird am Rotationsverdampfer zur Trockne gebracht. Der Rückstand wird in wenig siedendem Methanol aufgenommen, die Lösung wird filtriert und erneut zur Trockne gebracht. Der Rückstand wird aus ca. 15 ml Methanol umkristallisiert.

Ausbeute: 3,4 g 1-Aminomethyl-1-desoxynojirimycin (4) vom Schmelzpunkt 148-150°C. Nach erneuter Kristallisation aus Methanol steigt der Schmelzpunkt auf 154-155°C.

Beispiel 5

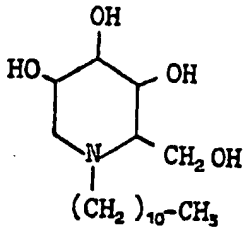



(5)

Zu 6,42 g 1-Aminomethyl-1-desoxynojirimycin in 100 ml Methanol und 20 ml Wasser tropft man bei -75°C 5,06 ml 6-Isocyanatohexansäurenitril zu. Es wird eine halbe Stunde bei -75°C gerührt. Dann läßt man langsam auf Raumtemperatur erwärmen (3 Stunden). Die Reaktionslösung wird eingeengt und der Rückstand aus Methanol kristallisiert.

Ausbeute : 4,8 g 1-(N'-5-Cyano-pentylureidomethyl)-1-desoxynojirimycin (5) vom Schmelzpunkt 160-165°C.

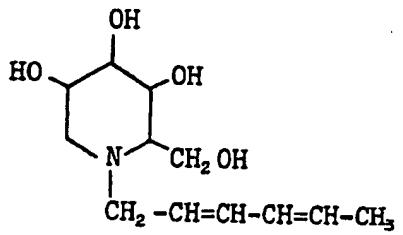
Beispiel 6




(6)

Die Herstellung erfolgt in Analogie zu Beispiel 2.
Schmelzpunkt : 162 °C.

Beispiel 7

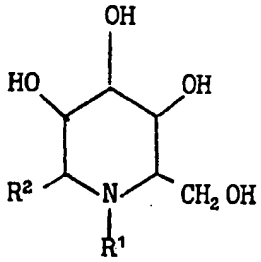


(7)

Zu 0,8 Mol Desoxynojirimycin und 1,12 Mol Kaliumcarbonat in 1,3 l Dimethylformamid gibt man unter Rühren bei Raumtemperatur 1,12 Mol Sorbylbromid. Dabei steigt die Temperatur auf 40°C. Man läßt 2,5 Stunden bei Raumtemperatur nachrühren, saugt die ausgefallenen Salze ab, nimmt das Filtrat in 2000 ml Wasser auf und extrahiert es zweimal mit je 500 ml Ether. Die Dimethylformamid/Wasser-Phase wird im Vakuum eingeengt, der Rückstand mit 1,4 l Aceton verrührt und der ausgefallene Feststoff abgesaugt. Dieser wird dann mit 1,5 l Ethanol ausgekocht und die restlichen Salze werden abfiltriert. Das Endprodukt kristallisiert aus, wird abgesaugt und aus Wasser umkristallisiert (14 ml Wasser auf 10 g Produkt). Man erhält in 30%-iger Ausbeute N-(Hexa-2,4-dienyl)-1-desoxynojirimycin (7) vom Schmelzpunkt 172-173°C.

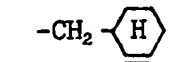
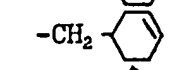
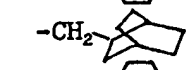
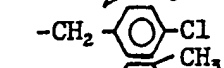
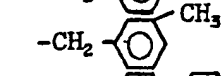
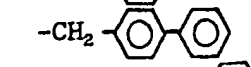
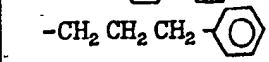
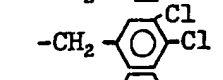
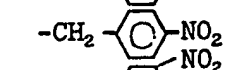
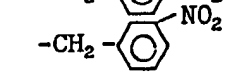
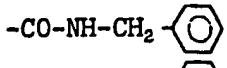
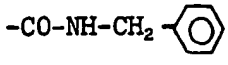
In analoger Weise und entsprechend den angegebenen Verfahrenweisen werden die Verbindungen der Formel (I) der nachfolgenden Tabelle 1 erhalten:

Tabelle 1

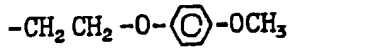
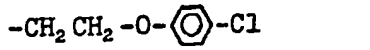
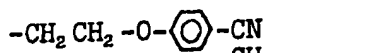
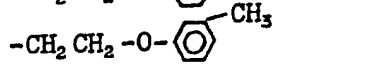
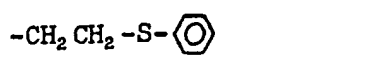
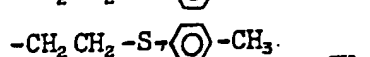
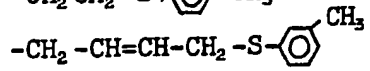
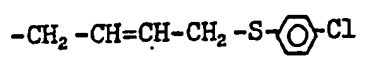
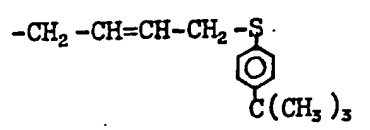
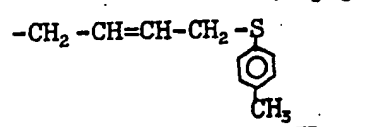
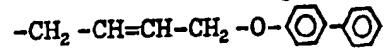
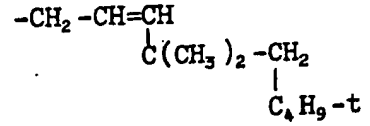


(I)

| Beispiel Nr. | $R^1$ | $R^2$ | Physikalische Konstante |
|---|---|---|---|
| 8 | $-CH_2-(CH_2)_5-CH_3$ | H | Fp:111-13°C |
| 9 | $-CH_2-C_6H_5$ | H | Fp:183-84°C |
| 10 | $-CH_2-C_5H_4N$ | H | Fp:174-75°C |
| 11 | $-CH_2-CH(OH)-CH_2OH$ | H | m/e=206,176 |
| 12 | $-CH_2CH_2CH_2-NH_2$ | H | m/e=189,146 |
| 13 | $-CH_2-COCH$ | H | Fp:187-88°C |
| 14 | $-CH_2-C_6H_4-NO_2$ | H | Rf-Wert=0,85* |
| 15 | $-CH_2-C_6H_4-COOH$ | H | Rf-Wert=0,7* |
| 16 | $-CH_2-C_6H_4-COOH$ | H | Fp:280-81°C |
| 17 | $-CH_2-CH_2-C_6H_5$ | H | Fp:179-81°C |
| 18 | $-(CH_2)_5-CH_3$ | H | Fp:112-13°C |
| 19 | $-(CH_2)_7-CH_3$ | H | Fp:115-17°C |
| 20 | $-(CH_2)_8-CH_3$ | H | Fp:105-07°C |

| Bsp. Nr. | $R^1$ | $R^2$ | Physikalische Konstante |
|---|---|---|---|
| 21 | $-(CH_2)_9-CH_3$ | H | Fp:151°C |
| 22 | $-(CH_2)_{11}-CH_3$ | H | Fp:164°C |
| 23 | $-(CH_2)_{13}-CH_3$ | H | Fp:105-07°C |
| 24 | $-(CH_2)_4-CH_2OH$ | H | Fp:86-87°C |
| 25 |  | H | Fp:138-40°C |
| 26 |  | H | Fp:142-44°C |
| 27 |  | H | Fp:160-62°C |
| 28 |  | H | Fp:153-55°C |
| 29 |  | H | Fp:134-36°C |
| 30 |  | H | Fp:240-45°C |
| 31 |  | H | Fp:125-27°C |
| 32 | $-CH_2-CH=CH_2$ | H | Fp:131-32°C |
| 33 | $-CH_2-C\equiv CH$ | H | Fp:160°C |
| 34 |  | H | Fp:130-32°C |
| 35 |  | H | Fp:144-46°C |
| 36 |  | H | Fp:168-70°C |
| 37 | $-CH_3$ | -CN | m/e:171,157,144 |
| 38 | H | -COOH | Fp:267-70°C |
| 39 | H | $-COOC_2H_5$ | Oel |
| 40 | $-CH_3$ | $-COOC_2H_5$ | m/e=218,200,176 |
| 41 | H | $-CONH_2$ | Fp:175-76°C |
| 42 | H |  | Fp:221-22°C |
| 43 | $-CH_3$ |  | Fp:229-30°C |
| 44 | H | $-CH_2-NH-CO-CH_3$ | Fp:168-71°C |

| Bsp. Nr. | $R^1$ | $R^2$ | Physikalische Konstante |
|---|---|---|---|
| 45 | $-CH_3$ | $-CH_2-NH-CO-CH_3$ | m/e:176,158 |
| 46 | H | $-CH_2-NH-CO-C_6H_5$ | Fp:216°C |
| 47 | $-CH_3$ | $-CH_2-NH-CO-C_6H_5$ | Fp:135-36°C |
| 48 | H | $-CH_2-NH-SO_2-C_6H_4-CH_3$ | Fp:173-75°C |
| 49 | $-CH_3$ | $-CH_2-NH-SO_2-C_6H_4-CH_3$ | Fp:218-19°C |
| 50 | H | $-CH_2-NH-CO-NH-C_6H_5$ | Fp:161-62°C |
| 51 | H | $-CH_2OH$ | m/e:162 |
| 52 | $-CH_2CH_2OCH_3$ | H | Rf-Wert:0,57* |
| 53 | $-CH_2CH_2-SCH_3$ | H | m/e:220,206,176 |
| 54 | $-CH_2CH_2-SC_2H_5$ | H | m/e:220,176 |
| 55 | $-CH_2CH_2OCH_2CH_2OCH_3$ | H | m/e:234,176 |
| 56 | $-(CH_2)_8-CH_3$ | $-CH_2-NH-COCH_3$ | m/e:329,288 |
| 57 | H | $-CH_2-NH-(CH_2)_8-CH(CH_3)_2$ | Rf-Wert:0,52* |
| 58 | $-CH_2CH_2-O-C_6H_5$ | H | Fp:140°C |
| 59 | $-(CH_2)_5-O-C_6H_5$ | H | Fp:138-39°C |
| 60 | $-(CH_2)_4-O-C_6H_5$ | H | Fp:110°C |
| 61 | $-CH_2CH_2-O-C_6H_3(CH_3)_2$ (2,6) | H | Fp:155-56°C |
| 62 | $-CH_2CH_2CH_2-O-C_6H_3(CH_3)_2$ (2,6) | H | Fp:128°C |
| 63 | $-CH_2CH_2-O-C_6H_3Cl_2$ (2,6) | H | Fp:175-76°C |
| 64 | $-(CH_2)_4-O-C_6H_5$ | H | Fp:152°C |
| 65 | $-CH_2-CH=CH-CH_2-O-C_6H_5$ | H | Fp:120°C($xH_2O$) |
| 66 | $-CH_2-CH=CH-CH_2-O-C_6H_4-CH_3$ | H | Fp:163-66°C |
| 67 | $-CH_2-CH=CH-CH_2-O-C_6H_4-COOC_2H_5$ | H | Harz |

| Bsp. Nr. | $R^1$ | $R^2$ | Physikalische Konstante |
|---|---|---|---|
| 68 |  | H | Fp:175-78°C |
| 69 |  | H | Fp:156-57°C |
| 70 |  | H | Fp:125°C |
| 71 |  | H | Fp:132-34°C |
| 72 |  | H | Fp:121-23°C |
| 73 |  | H | Fp:126-27°C |
| 74 |  | H | Fp:106°C |
| 75 |  | H | Fp:93-95°C |
| 76 |  | H | Fp:138-40°C |
| 77 |  | H | Fp: ≥83°C |
| 78 |  | H | Fp:165-69°C |
| 79 | $-CH_2-(CH=CH)_2-C_2H_5$ | H | Fp:135-37°C |
| 80 | $-CH_2-CH=CH-CH_3$ | H | Fp:120-23°C |
| 81 |  | H | Fp:112-18°C |

* Rf-Werte bestimmt auf DC-Fertigplatten der Firma Merck, Kieselgel 60; Fließmittel: Essigester/Methanol/$H_2O$/25 %ige wäßr. Ammoniak = 100/60/40/2 (Volumenteile). - Zum Vergleich: Rf-Wert von 1-Desoxynojirimycin (A) = 0,3.

Die erfindungsgemäßen Wirkstoffe beeinflussen das Pflanzenwachstum und können deshalb als Defoliants, Desiccants, Krautabtötungsmittel, Keimhemmungsmittel und insbesondere als Unkrautvernichtungsmittel verwendet werden. Unter Unkraut im weitesten Sinne sind alle Pflanzen zu verstehen, die an Orten aufwachsen, wo sie unerwünscht sind. Ob die erfindungsgemäßen Stoffe als totale oder selektive Herbizide wirken, hängt im wesentlichen von der angewendeten Menge ab.

Die erfindungsgemäßen Wirkstoffe können z.B. bei den folgenden Pflanzen verwendet werden:

Dikotyle Unkräuter der Gattungen: Sinapis, Lepidium, Galium, Stellaria, Matricaria, Anthemis, Galinsoga, Chenopodium, Urtica, Senecio, Amaranthus, Portulaca, Xanthium, Convolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindernia, Lamium, Veronica, Abutilon, Emex, Datura, Viola, Galeopsis, Papaver, Centaurea.

Monokotyle Unkräuter der Gattungen: Echinochloa, Setaria, Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, Sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Paspalum, Ischaemum, Sphenoclea, Dactyloctenium, Agrostis, Alopecurus, Apera.

Monokotyle Kulturen der Gattungen: Oryza, Zea, Triticum,

Hordeum, Avena, Secale, Sorghum, Panicum, Saccharum, Ananas, Asparagus, Allium.

Die Verwendung der erfindungsgemäßen Wirkstoffe ist jedoch keineswegs auf diese Gattungen beschränkt, sondern erstreckt sich in gleicher Weise auch auf andere Pflanzen.

Die Verbindungen eignen sich in Abhängigkeit von der Konzentration zur Totalunkrautbekämpfung z.B. auf Industrie- und Gleisanlagen und auf Wegen und Plätzen mit und ohne Baumbewuchs. Ebenso können die Verbindungen zur Unkrautbekämpfung in Dauerkulturen z.B. Forst-, Ziergehölz-, Obst-, Wein-, Citrus-, Nuss-, Bananen-, Kaffee-, Tee-, Gummi-, Ölpalm-, Kakao-, Beerenfrucht- und Hopfenanlagen und zur selektiven Unkrautbekämpfung in einjährigen Kulturen eingesetzt werden.

Die erfindungsgemäßen Wirkstoffe können als solche oder in ihren Formulierungen auch in Mischung mit bekannten Herbiziden zur Unkrautbekämpfung Verwendung finden, wobei Fertigformulierung oder Tankmischung möglich ist.

Die Wirkstoffe können in die üblichen Formulierungen übergeführt werden, wie Lösungen, Emulsionen, Suspensionen, Pulver, Schäume, Pasten, Granulate, Wirkstoffimprägnierte Natur- und synthetische Stoffe und Feinstverkapselungen in polymeren Stoffen.

Diese Formulierungen werden in bekannter Weise herge-

stellt, z.B. durch Vermischen der Wirkstoffe mit Steckmitteln, also flüssigen Lösungsmitteln und/oder festen Trägerstoffen, gegebenenfalls unter Verwendung von oberflächenaktiven Mitteln, also Emulgiermitteln und/oder Dispergiermitteln und/oder schaumerzeugenden Mitteln. Im Falle der Benutzung von Wasser als Streckmittel können z.B. auch organische Lösungsmittel als Hilfslösungsmittel verwendet werden. Als flüssige Lösungsmittel kommen im wesentlichen in Frage: Aromaten, wie Xylol, Toluol, oder Alkylnaphthaline, chlorierte Aromaten oder chlorierte aliphatische Kohlenwasserstoffe, wie Chlorbenzole, Chlorethylene oder Methylenchlorid, aliphatische Kohlenwasserstoffe, wie Cyclohexan oder Paraffine, z.B. Erdölfraktionen, Alkohole, wie Butanol oder Glykol sowie deren Ether und Ester, Ketone, wie Aceton, Methylethylketon, Methylisobutylketon oder Cyclohexanon, stark polare Lösungsmittel, wie Dimethylformamid und Dimethylsulfoxid, sowie Wasser.

Als feste Trägerstoffe kommen in Frage:

Z.B. natürliche Gesteinsmehle, wie Kaoline, Tonerden, Talkum, Kreide, Quarz, Attapulgit, Montmorillonit oder Diatomeenerde und synthetische Gesteinsmehle, wie hochdisperse Kieselsäure, Aluminiumoxid und Silikate; als feste Trägerstoffe für Granulate kommen in Frage: z.B. gebrochene und fraktionierte natürliche Gesteine wie Calcit, Marmor, Bims, Sepiolith, Dolomit sowie synthetische Granulate aus anorganischen und organischen Mehlen sowie Granulate aus organischem Material wie Säge-

mehl, Kokosnußschalen, Maiskolben und Tabakstengel; als Emulgier- und/oder schaumerzeugende Mittel kommen in Frage: z.B. nichtionogene und anionische Emulgatoren, wie Polyoxyethylen-Fettsäure-Ester, Polyoxyethylen-Fettalkohol-Ether, z.B. Alkylarylpolyglykol-ether, Alkylsulfonate, Alkylsulfate, Arylsulfonate sowie Eiweißhydrolysate; als Dispergiermittel kommen in Frage: z.B. Lignin-Sulfitablaugen und Methylcellulose.

Es können in den Formulierungen Haftmittel wie Carboxymethylcellulose, natürliche und synthetische pulverige, körnige oder latexförmige Polymere verwendet werden, wie Gummiarabicum, Polvinylalkohol, Polyvinylacetat.

Es können Farbstoffe wie anorganische Pigmente, z.B. Eisenoxid, Titanoxid, Ferrocyanblau und organische Farbstoffe, wie Alizarin-, Azol-, Metallphthalocyaninfarbstoffe und Spurennährstoffe wie Salze von Eisen, Mangan, Bor, Kupfer, Kobalt, Molybdän und Zink verwendet werden.

Die Formulierungen enthalten im allgemeinen zwischen 0,1 und 95 Gewichtsprozent Wirkstoff, vorzugsweise zwischen 0,5 und 90 %.

Die erfindungsgemäß verwendbaren Wirkstoffe können als solche oder in ihren Formulierungen auch in Mischung mit bekannten Herbiziden zur Unkrautbekämpfung Verwendung finden, wobei Fertigformulierung oder Tankmischung möglich ist. Auch eine Mischung mit anderen bekannten Wirkstoffen, wie Fungiziden, Insektiziden, Akariziden,

Nematiziden, Schutzstoffen gegen Vogelfraß, Wuchsstoffen, Pflanzennährstoffen und Bodenstrukturverbesserungsmitteln ist möglich.

Die Wirkstoffe können als solche, in Form ihrer Formulierungen oder der daraus durch weiteres Verdünnen bereiteten Anwendungsformen, wie gebrauchsfertige Lösungen, Suspensionen, Emulsionen, Pulver, Pasten und Granulate angewandt werden. Die Anwendung geschieht in üblicher Weise, z.B. durch Gießen, Spritzen, Sprühen, Streuen.

Die erfindungsgemäßen Wirkstoffe können sowohl vor als auch nach dem Auflaufen der Pflanzen appliziert werden. Die Anwendung wird vorzugsweise vor dem Auflaufen der Pflanzen, also im pre-emergence-Verfahren, vorgenommen. Sie können auch vor der Saat in den Boden eingearbeitet werden.

Die aufgewandte Wirkstoffmenge kann in größeren Bereichen schwanken. Sie hängt im wesentlichen von der Art des gewünschten Effekts ab. Im allgemeinen liegen die Aufwandmengen zwischen 0,1 und 50 kg Wirkstoff pro ha, vorzugsweise zwischen 1 und 40 kg/ha.

Verwendungsbeispiele

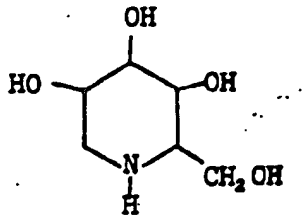
Pre-emergence-Test:

In Schalen, die mit Vermiculite gefüllt sind, werden Samen von Lepidium (LEPSA), Echinochloa (ECHCG), Stellaria (STEME), Portulaca (POROL) und Poa (POAAN) ausgelegt. Die Schalen werden dann mit einer Hoagland-Nährlösung gegossen, der die erfindungsgemäßen Wirkstoffe und die bekannte Verbindung (A) in bestimmten Mengen zugesetzt sind. Nach 2 Wochen wird der Schädigungsgrad der Pflanzen im Vergleich zu den unbehandelten Pflanzen bonitiert. Es bedeuten:

0 % = keine Wirkung (wie unbehandelte Kontrolle);
100 % = totale Vernichtung;
H = Hemmung.

Wirkstoffe, Aufwandmengen und Resultate gehen aus der nachfolgenden Tabelle 2 hervor.

Als Vergleichsmittel dient die bekannte Verbindung (A) der Formel:




(A)

2-Hydroxymethyl-3,4,5-trihydroxy-piperidin (=1-Desoxy-nojirimycin).

Tabelle 2

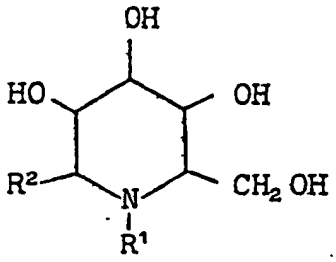
Pre-emergence-Test / Gewächshaus

| Wirkstoffe (vgl. Herstellungsbeispiele) | Aufwandmenge kg/ha | % Abtötung | | | | |
|---|---|---|---|---|---|---|
| | | Lepidium | Echinochloa | Stellaria | Portulaca | Poa |
| (A) (bekannt) | 40 | 100 | 0 | 0 | 30/H | 30/H |
| (1) | 40 | 100 | 70 | 40 | 100 | 100 |
| (2) | 40 | 100 | 85 | 80 | 100 | 95 |
| (5) | 40 | 85 | 0 | 20/H | 20/H | 50/H |
| (6) | 40 | 85 | 40/H | 80 | 40/H | 20/H |
| (7) | 40 | 80 | 40/H | 0 | 0 | 80 |

English translation of DE 3024901

Claims

1) Herbicides, characterized in that they contain at least one 2-hydroxymethyl-3,4,5-trihydroxy-piperidine derivative of the general formula




(I)

in which

$R^1$ represents alkyl with more than 4 carbon atoms, alkenyl, alkadienyl, alkinyl, hydroxyalkyl and the $-X-R^3$ grouping, wherein

X represents alkylene or alkenylene and

$R^3$ represents optionally substituted aryl, optionally substituted aryloxy, optionally substituted arylmercapto, optionally substituted pyridyl, alkoxy, alkoxy-alkoxy, alkylthio, amino, hydroxycarbonyl, optionally substituted cycloalkyl and optionally substituted cycloalkenyl,

$R^1$ also represents hydrogen or alkyl with 1 to 4 carbon atoms if $R^2$ represents a residue other than hydrogen,

$R^2$ represents hydrogen, cyano, hydroxy, hydroxymethyl, hydroxysulphonyl, aminomethyl,

alkylaminomethyl, hydroxycarbonyl, alkoxycarbonyl and the $-CO-NH-R^4$, $-CH_2-NH-CO-R^5$, $-CH_2-NH-SO_2-R^5$, $-CH_2-NH-CO(S)-NH-R^5$ and $-CH_2-NH-CO-OR^5$ groupings, wherein

$R^4$ represents hydrogen, alkyl or optionally substituted aralkyl and

$R^5$ represents alkyl, optionally substituted aryl, optionally substituted aralkyl, cyanalkyl, aminoalkyl or halogenalkyl.

2) Method of weed control, characterized in that 2-hydroxymethyl-3,4,5-trihydroxy-piperidine derivatives according to formula (I) in claim 1 are allowed to act on the weeds or their habitat.

3) Use of 2-hydroxymethyl-3,4,5-trihydroxy-piperidine derivatives according to formula (I) in claim 1 for weed control.

4) Process for the preparation of herbicides, characterized in that 2-hydroxymethyl-3,4,5-trihydroxy-piperidine derivatives according to formula (I) in claim 1 are mixed with extenders and/or surfactants.

BAYER AKTIENGESELLSCHAFT 5090 Leverkusen-Bayerwerk

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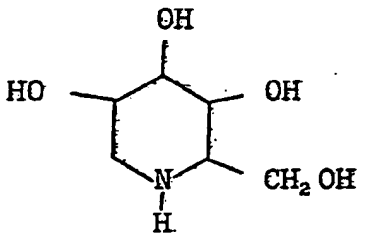
IIa

Herbicides based on piperidine derivatives

The present invention relates to the use of widely known 1- and/or 6-substituted 2-hydroxymethyl-3,4,5-trihydroxy-piperidine derivatives (=N- and/or 1-substituted 1-deoxynojirimycin derivatives) as herbicides.

It has already become known that pharmacologically active 2-hydroxymethyl-3,4,5-trihydroxy-piperidine (=1-deoxynojirimycin) of the formula

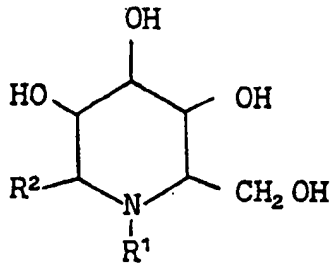



(A)

(cf. DE-OS 26 56 602) also has a herbicidal effect (cf. published JP patent application no. 55-7224). However, 1-deoxynojirimycin is only a relatively weak herbicide which displays no satisfactory effect in particular against certain important weeds.

In addition, it is known that certain further 3,4,5-trihydroxy-piperidine derivatives can be used as medicinal products (cf. DE-OS 27 58 025; published EP patent application no. 0 000 947). However, no herbicidal effectiveness of these compounds is described.

It has now been found that 2-hydroxymethyl-3,4,5-trihydroxy-piperidine derivatives of the general formula



(I)

in which

$R^1$ represents alkyl with more than 4 carbon atoms, alkenyl, alkadienyl, alkinyl, hydroxyalkyl and the $-X-R^3$ grouping, wherein

X represents alkylene or alkenylene and

$R^3$ represents optionally substituted aryl, optionally substituted aryloxy, optionally substituted arylmercapto, optionally substituted pyridyl, alkoxy, alkoxy-alkoxy, alkylthio, amino, hydroxycarbonyl, optionally substituted cycloalkyl and optionally substituted cycloalkenyl,

$R^1$ also represents hydrogen or alkyl with 1 to 4 carbon atoms if $R^2$ represents a residue other than hydrogen,

$R^2$ represents hydrogen, cyano, hydroxy, hydroxymethyl, hydroxysulphonyl, aminomethyl, alkylaminomethyl, hydroxycarbonyl, alkoxycarbonyl and the $-CO-NH-R^4$, $-CH_2-NH-CO-R^5$, $-CH_2-NH-SO_2-R^5$, $-CH_2-NH-CO(S)-NH-R^5$ and $-CH_2-NH-CO-OR^5$ groupings, wherein

$R^4$ represents hydrogen, alkyl or optionally substituted aralkyl, and

$R^5$ represents alkyl, optionally substituted aryl, optionally substituted aralkyl, cyanalkyl, aminoalkyl or halogenalkyl,

have good herbicidal properties.

The compounds of formula (I) can optionally be present as geometric and/or optical isomers. The present invention covers both the individual isomers and the isomer mixtures.

Surprisingly, the 2-hydroxymethyl-3,4,5-trihydroxy-piperidine derivatives of formula (I) which can be used according to the invention display a considerably greater herbicidal effect than the 1-deoxynojirimycin known from the state of the art which is the closest compound in terms of chemistry and effect. The use according to the invention of the substances of formula (I) thus represents an enrichment of the art.

The 2-hydroxymethyl-3,4,5-trihydroxy-piperidine derivatives which can be used according to the invention are generally defined by formula (I). In this formula, $\underline{R}^1$ preferably represents straight-chain or branched alkyl with 5 to 18 carbon atoms, alkenyl with 2 to 12 carbon atoms, alkadienyl with 4 to 8 carbon atoms, alkinyl with 2 to 6 carbon atoms, hydroxyalkyl with 1 to 6 carbon atoms and 1 to 3 hydroxy groups, and the $-X-R^3$ grouping. In addition, $\underline{R}^1$ also preferably represents hydrogen or alkyl with 1 to 4 carbon atoms if $R^2$ represents a residue other than hydrogen.

X preferably represents a straight-chain or branched alkylene chain with 1 to 12 carbon atoms or a straight-chain or branched alkenylene chain with 2 to 12 carbon atoms.

$R^3$ preferably represents optionally substituted aryl, aryloxy and arylmercapto with in each case 6 to 10 carbon atoms, wherein the following may be preferably named as substituents: halogen, alkyl with 1 to 4 carbon atoms, halogenalkyl with 1 to 2 carbon atoms and 1 to 5 identical or different halogen atoms, alkoxy, alkylthio and alkylsulphonyl with 1 to 4 carbon atoms each, hydroxy, cyano, nitro, amino, alkylamino, dialkylamino and alkylcarbonylamino with in each case 1 to 2 carbon atoms per alkyl residue, hydroxycarbonyl (-COOH), alkoxycarbonyl with 1 to 4 carbon atoms in the alkyl residue, and phenoxy, benzyl and phenyl optionally substituted by halogen.

Furthermore, $R^3$ preferably represents pyridyl optionally substituted by halogen and alkyl with 1 to 2 carbon atoms, alkoxy, alkoxy-alkoxy and alkylthio with 1 to 4 carbon atoms per alkyl part, amino, hydroxycarbonyl, alkoxycarbonyl with 1 to 4 carbon atoms in the alkyl part, and cycloalkyl optionally substituted by alkyl with 1 to 4 carbon atoms and cycloalkenyl with in each case 5 to 7 carbon atoms.

$R^2$ preferably represents hydrogen, cyano, hydroxy, hydroxymethyl, hydroxysulphonyl, hydroxycarbonyl, aminomethyl, alkylaminomethyl with 1 to 4 carbon atoms in the alkyl part, alkoxycarbonyl with 1 to 4 carbon atoms,

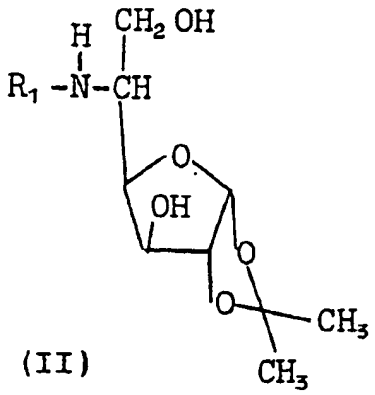
and the $-CO-NH-R^4$, $-CH_2-NH-CO-R^5$, $-CH_2-NH-SO_2-R^5$, $-CH_2-NH-CO(S)-NH-R^5$ and $-CH_2-NH-CO-OR^5$ groupings.

$R^4$ preferably represents hydrogen, alkyl with 1 to 4 carbon atoms, and optionally substituted aralkyl with 6 to 10 carbon atoms in the aryl part and 1 to 4 carbon atoms in the alkyl part, wherein the substituents already named above in the definition of the residue $R^3$ preferably come into consideration as aryl substituents.

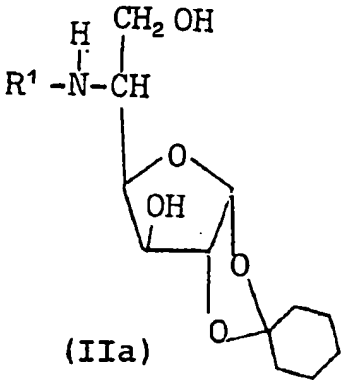
$R^5$ preferably represents alkyl with 1 to 12 carbon atoms, cyanalkyl and aminoalkyl with 1 to 12 carbon atoms per alkyl part, halogenalkyl with 1 to 4 carbon atoms and 1 to 5 identical or different halogen atoms, and optionally substituted aryl and aralkyl with in each case 6 to 10 carbon atoms in the aryl part and 1 to 4 carbon atoms in the alkyl part, wherein the substituents already named above in the definition of the residue $R^3$ preferably come into consideration as substituents.

By halogen is preferably meant in each case chlorine and fluorine.

Some of the active ingredients to be used according to the invention are known (cf. EP 0 000 947), some are the subject of separate earlier patent applications (cf. German patent applications P 29 25 943.6 and P 30 07 078.1). The compounds of formula (I) can be prepared using the processes given there. Thus, compounds of formula (I) with $R^2$ = OH are obtained by removing the isopropylidene or cyclohexylidene protective groups from compounds of formula (II) or (IIa)



(II)



(IIa)

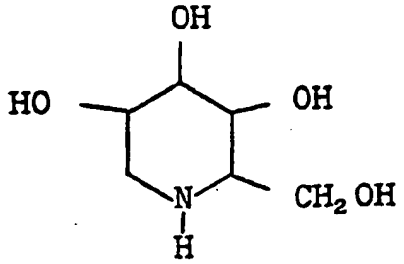
in which $R^1$ has the meaning given above,

by careful acid hydrolysis, wherein it is possibly expedient to collect the compounds of formula (I), formed by ring extension, with $R^2$ = OH in the form of adducts of sulphuric acid or hydrogen cyanide ($R^2$ = $-OSO_2H$ or CN). The compounds of formula (I) with $R^2$ = OH are released from the bisulphite addition products (i.e. acid sulphuric acid esters) by treatment with bases, preferably alkaline earth hydroxides such as $Ca(OH)_2$ or $Sr(OH)_2$, but in particular $Ba(OH)_2$. The compounds of formula (I) with $R^2$=H are obtained from the compounds of formula (I) with $R^2$=OH by reaction with hydrogen donor reducing agents, such as for example $NaBH_4$.

Certain compounds of formula (I) can also be obtained if the compounds of formula (I) with $R^2$=OH are converted to compounds of formula (I) with $R^2$=CN in a manner known per se with hydrogen cyanide and compounds with $R^2$= $-CH_2NH_2$ are optionally prepared from these by catalytic hydrogenation of the nitrile group, and the amino group is optionally acylated, sulphonylated, alkylated, or derivatized with chloroformic acid esters, isocyanates or mustard oils in a manner known per se to form compounds in which $R^2$= $-CH_2-NH-CO-R^5$ or is alkylamino.

The compounds of formula (I) in which $R^2$= -COOH are obtained by hydrolyzing compounds of formula (I) with $R^2$= -CN in a manner known per se. Compounds of formula (I) with $R^2$= -COO alkyl can be obtained from the thus obtained carboxylic acids in a manner known per se by reaction with corresponding alcohols, compounds of formula (I) with $R^2$= -CONHR$^4$ by aminolysis of the esters with amines of the general formula $R^4$-$NH_2$.

N-substituted compounds of formula (I) with $R^2$=H are also obtained if the compound of formula (III), i.e. 1-deoxynojirimycin,




(III) = (A)

is reacted either with aldehydes of the formula

$$O = CH - R^1 \qquad (IV)$$

in which

$R^1$ has the meaning given above,

in the presence of a hydrogen donor reducing agent, or

in the usual manner with reactive alkylating agents of the formula

$$Z - R^1 \qquad (V)$$

in which

$R^1$ has the meaning given above and

Z represents halogen or the $-OSO_3$ group.

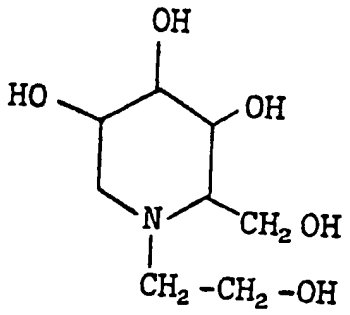
Instead of the compounds of formula (V), other reactive alkylating agents, such as e.g. ethylene oxide, can also be used.

Further details of the different procedures can be found in published EP patent application no. 0 000 947 and also in the following preparation examples.

The starting products of formulae (II), (IIa), (III), (IV) and (V) are generally known compounds of organic chemistry, or they and their preparation are described in EP patent application no. 0 000 947.

Preparation examples:

Example 1

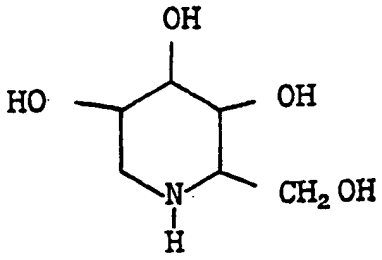



(1)

90.0 g of 1-deoxynojirimycin (A) was dissolved in 450 ml of $H_2O$ and saturated with $CO_2$ at 5°C. The mixture was stirred at 20°C for 20 hours, then cooled to 5°C and saturated with $CO_2$ again. 27.97 g of ethylene oxide was weighed out in liquid form and added all at once. The reaction mixture was stirred at 5°C to 10°C for 30 minutes, then heated to 50°C within 30 minutes and stirred at 50°C for 6 hours. The mixture was worked up after a further 20 hours of stirring at 20°C. The reaction mixture was concentrated on the rotary evaporator, the residue was brought to the boil with 2-methoxyethanol and clarified with activated carbon. The product was left to crystallize out at 20°C. Extraction by suction, with 2-methoxyethanol, followed, then rewashing with ethanol and drying. The thus-obtained 84.2 g of N-(ß-hydroxyethyl)-1-deoxynojirimycin with a melting point of 144-145.5°C was recrystallized from 90% ethanol. Yield of N-(ß-hydroxyethyl)-1-deoxynojirimycin (1): 78.3 g with a melting point of 147-149°C.

The compound (1) can also be called 1-(ß-hydroxyethyl)-2-hydroxymethyl-3,4,5-trihydroxy-piperidine.

Preparation of the starting product

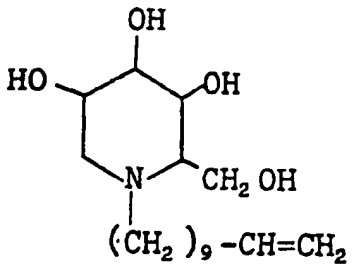


(A)

A solution of 2 g of 5-amino-5-deoxy-1,2-isopropylidene-α-D-glucofuranose in 8 ml of 2 N hydrochloric acid is stirred for 24 hours. The mixture is diluted with 5 ml of water and, after addition of 0.69 g of triethylamine and 0.3 g of Raney nickel, hydrogenated at 3.5 bar for 5 hours. It is filtered out of the catalyst, concentrated in a vacuum and concentrated twice more in each case after addition of a little ethanol, wherein crystallization occurs. The crystals are stirred with ethanol, extracted by suction and washed thoroughly with ethanol. 1.45 g (79.7% of theory) of 1-deoxynojirimycin hydrochloride (A) with a melting point of 209-210°C is obtained accompanied by decomposition.

The free base is obtained in the usual manner from the hydrochloride.

Example 2

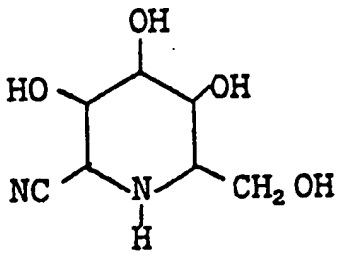


(2)

17 ml of 10-undecenol and 3 g of sodium cyanoborohydride ($NaCNBH_3$) are added to 7.4 g of 1-deoxynojirimycin in 150

ml of methanol and 6.7 ml of glacial acetic acid. The mixture is stirred at room temperature for 2 hours. The reaction mixture is then deposited on a column filled with strongly acidic ion exchanger ($H^{\oplus}$ form). Elimination follows, first with methanol/water=2:1, then with ethanol/6% ammonia=2:1. The ammoniacal eluate is concentrated. The remainder is crystallized from water. Yield: 11.7 g of N-undecen-10-yl-1-deoxynojirimycin (2) with a melting point of 144-146°C.

Example 3

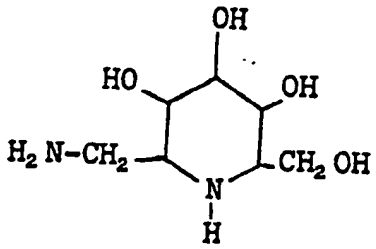



(3)

17.5 g of nojirimycin bisulphite adduct is added to 200 ml of water and 21.2 g of $Ba(OH)_2 \times H_2O$. The mixture is stirred at room temperature for one hour and the solid matter is extracted by suction. 12 ml of liquid hydrogen cyanide is added to the filtrate and the mixture stirred for 1/2 hour. The solution is filtered again and concentrated to 20 ml on the rotary evaporator. 20 ml of methanol is added next, wherein the desired product starts to crystallize out, and the crystallization is completed by adding 100 ml of ethanol. The precipitate is extracted by suction.

Yield: 12.0 g of 1-cyano-1-deoxynojirimycin (3) with a melting point of 152-153°C. After recrystallization from methanol and a little water, the substance melts at 155-156°C.

Example 4

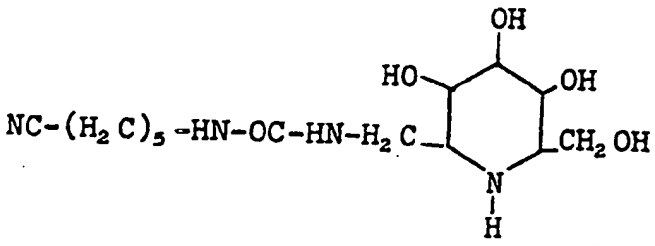


(4)

5 g of 1-cyano-1-deoxynojirimycin (example 3) is hydrogenated in 100 ml of water with 10 g of Raney nickel as catalyst for one hour at 3.5 atmospheres $H_2$ pressure in a vibrating pear-shaped flask. Extraction from the catalyst by suction then follows and the solution is dried on the rotary evaporator. The residue is taken up in a little boiling methanol, the solution is filtered and dried again. The residue is recrystallized from approx. 15 ml of methanol.

Yield: 3.4 g of 1-aminomethyl-1-deoxynojirimycin (4) with a melting point of 148-150°C. After renewed crystallizing from methanol, the melting point increases to 154-155°C.

Example 5



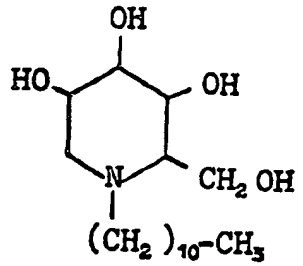
(5)

5.06 ml of 6-isocyanato-hexanoic acid nitrile is added dropwise at -75°C to 6.42 g of 1-aminomethyl-1-deoxynojirimycin in 100 ml of methanol and 20 ml of water. The mixture is stirred at -75°C for half an hour and then heated slowly to room temperature (3 hours). The reaction

solution is concentrated and the remainder crystallized from methanol.

Yield: 4.8 g of 1-(N'-5-cyanopentylureidomethyl)-1-deoxynojirimycin (5) with a melting point of 160-165°C.

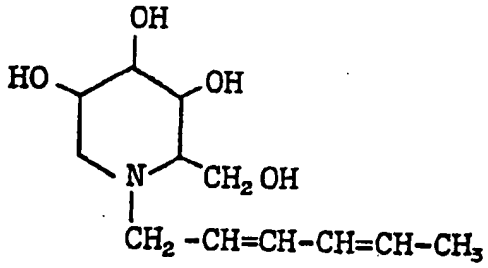
Example 6




(6)

The preparation is analogous to example 2. Melting point: 162°C.

Example 7



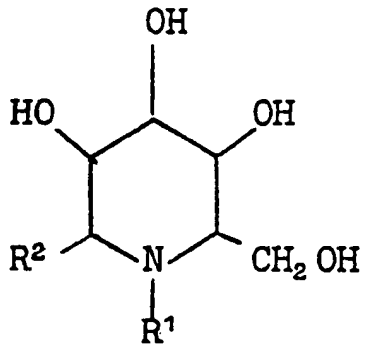

(7)

1.12 mol of sorbyl bromide is added to 0.8 mol of deoxynojirimycin and 1.12 mol of potassium carbonate in 1.3 l of dimethylformamide at room temperature accompanied by stirring. The temperature increases to 40°C. Stirring continues for 2.5 hours at room temperature, the precipitated salts are extracted by suction, the filtrate is taken up in 2000 ml of water and extracted twice with 500 ml of ether each time. The dimethylformamide/water phase is concentrated in a vacuum, the residue is stirred with 1.4 l of acetone and the precipitated solid matter is extracted by suction. This

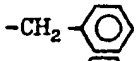
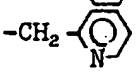
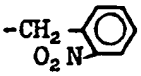
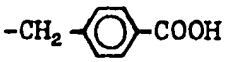
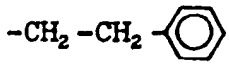
is then boiled out with 1.5 l of ethanol and the remaining salts are filtered off. The end product crystallizes out, is extracted by suction and recrystallized from water (14 ml of water per 10 g of product). A 30% yield of N-(hexa-2,4-dienyl)-1-deoxynojirimycin (7) with a melting point of 172-173°C is obtained.

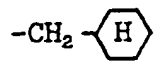
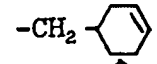
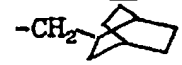
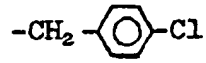
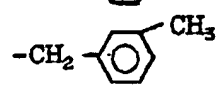
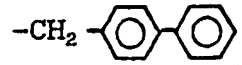
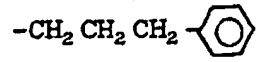
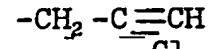
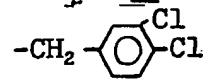
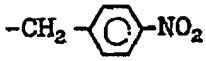
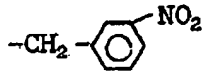
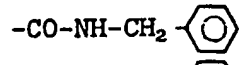
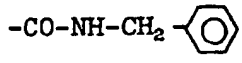
The compounds of formula (I) of table 1 below are obtained in an analogous manner and according to the given procedures:

Table 1

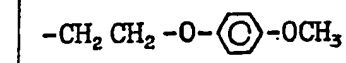
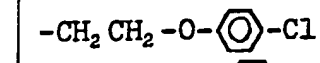
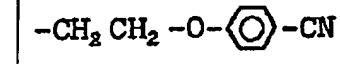
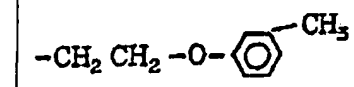
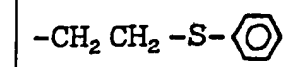
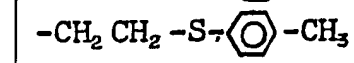
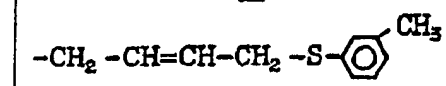
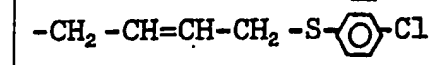
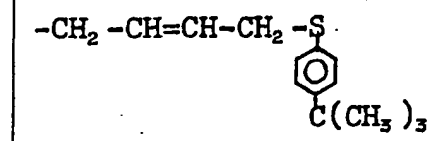
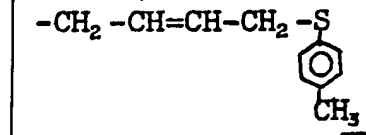
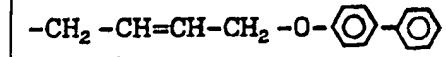
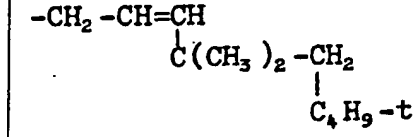


(I)

| Example no. | $R^1$ | $R^2$ | Physical constant |
|---|---|---|---|
| 8 | $-CH_2-(CH_2)_5-CH_3$ | H | mp:111-13°C |
| 9 |  | H | mp:183-84°C |
| 10 |  | H | mp:174-75°C |
| 11 | $-CH_2-CH(OH)-CH_2OH$ | H | m/e=206,176 |
| 12 | $-CH_2CH_2CH_2-NH_2$ | H | m/e=189,146 |
| 13 | $-CH_2-COOH$ | H | mp:187-88°C |
| 14 |  | H | Rf value=0.85* |
| 15 |  | H | Rf value=0.7* |
| 16 |  | H | mp:280-81°C |
| 17 |  | H | mp:179-81°C |
| 18 | $-(CH_2)_5-CH_3$ | H | mp:112-13°C |
| 19 | $-(CH_2)_7-CH_3$ | H | mp:115-17°C |
| 20 | $-(CH_2)_8-CH_3$ | H | mp:105-07°C |

| Example no. | $R^1$ | $R^2$ | Physical constant |
|---|---|---|---|
| 21 | $-(CH_2)_9-CH_3$ | H | mp:151°C |
| 22 | $-(CH_2)_{11}-CH_3$ | H | mp:164°C |
| 23 | $-(CH_2)_{13}-CH_3$ | H | mp:105-07°C |
| 24 | $-(CH_2)_4-CH_2OH$ | H | mp:86-87°C |
| 25 |  | H | mp:138-40°C |
| 26 |  | H | mp:142-44°C |
| 27 |  | H | mp:160-62°C |
| 28 |  | H | mp:153-55°C |
| 29 |  | H | mp:134-36°C |
| 30 |  | H | mp:240-45°C |
| 31 |  | H | mp:125-27°C |
| 32 | $-CH_2-CH=CH_2$ | H | mp:131-32°C |
| 33 |  | H | mp:160°C |
| 34 |  | H | mp:130-32°C |
| 35 |  | H | mp:144-46°C |
| 36 |  | H | mp:168-70°C |
| 37 | $-CH_3$ | -CN | m/e:171,157,144 |
| 38 | H | -COOH | mp:267-70°C |
| 39 | H | $-COOC_2H_5$ | oil |
| 40 | $-CH_3$ | $-COOC_2H_5$ | m/e=218,200,176 |
| 41 | H | $-CONH_2$ | mp:175-76°C |
| 42 | H |  | mp:221-22°C |
| 43 | $-CH_3$ |  | mp:229-30°C |
| 44 | H | $-CH_2-NH-CO-CH_3$ | mp:168-71°C |

| Example no. | $R^1$ | $R^2$ | Physical constant |
|---|---|---|---|
| 45 | $-CH_3$ | $-CH_2-NH-CO-CH_3$ | m/e:176,158 |
| 46 | H | $-CH_2-NH-CO-C_6H_5$ | mp:216°C |
| 47 | $-CH_3$ | $-CH_2-NH-CO-C_6H_5$ | mp:135-36°C |
| 48 | H | $-CH_2NH-SO_2-C_6H_4-CH_3$ | mp:173-75°C |
| 49 | $-CH_3$ | $-CH_2NH-SO_2-C_6H_4-CH_3$ | mp:218-19°C |
| 50 | H | $-CH_2NH-CO-NH-C_6H_5$ | mp:161-62°C |
| 51 | H | $-CH_2OH$ | m/e:162 |
| 52 | $-CH_2CH_2OCH_3$ | H | Rf value:0.57* |
| 53 | $-CH_2CH_2-SCH_3$ | H | m/e:220,206,176 |
| 54 | $-CH_2CH_2-SC_2H_5$ | H | m/e:220,176 |
| 55 | $-CH_2CH_2OCH_2CH_2OCH_3$ | H | m/e:234,176 |
| 56 | $-(CH_2)_8-CH_3$ | $-CH_2-NH-COCH_3$ | m/e:329,288 |
| 57 | H | $-CH_2-NH-(CH_2)_8-CH(CH_3)$ | Rf value:0.52* |
| 58 | $-CH_2CH_2-O-C_6H_5$ | H | mp:140°C |
| 59 | $-(CH_2)_5-O-C_6H_5$ | H | mp:138-39°C |
| 60 | $-(CH_2)_4-O-C_6H_5$ | H | mp:110°C |
| 61 | $-CH_2CH_2-O-C_6H_3(CH_3)_2$ (2,6) | H | mp:155-56°C |
| 62 | $-CH_2CH_2CH_2-O-C_6H_3(CH_3)$ (2) | H | mp:128°C |
| 63 | $-CH_2CH_2-O-C_6H_3Cl_2$ (2,4) | H | mp:175-76°C |
| 64 | $-(CH_2)_4-O-C_6H_5$ | H | mp:152°C |
| 65 | $-CH_2-CH=CH-CH_2-O-C_6H_5$ | H | mp:120°C(x$H_2O$) |
| 66 | $-CH_2-CH=CH-CH_2-O-C_6H_4-CH_3$ | H | mp:163-66°C |
| 67 | $-CH_2-CH=CH-CH_2-O-C_6H_4-COOC_2H_5$ | H | resin |

| Example no. | $R^1$ | $R^2$ | Physical constant |
|---|---|---|---|
| 68 |  | H | mp:175-78°C |
| 69 |  | H | mp:156-57°C |
| 70 |  | H | mp:125°C |
| 71 |  | H | mp:132-34°C |
| 72 |  | H | mp:121-23°C |
| 73 |  | H | mp:126-27°C |
| 74 |  | H | mp:106°C |
| 75 |  | H | mp:93-95°C |
| 76 |  | H | mp:138-40°C |
| 77 |  | H | mp:≥83°C |
| 78 |  | H | mp:165-69°C |
| 79 | $-CH_2-(CH=CH)_2-C_2H_5$ | H | mp:135-37°C |
| 80 | $-CH_2-CH=CH-CH_3$ | H | mp:120-23°C |
| 81 |  | H | mp:112-18°C |

* Rf values determined on Merck TLC plates, silica gel 60; mobile solvent: ethyl acetate/methanol/$H_2O$/25% aqueous ammonia = 100/60/40/2 (parts by volume). -For comparison: Rf value of 1-deoxynojirimycin (A) = 0.3.

The active ingredients according to the invention affect plant growth and can therefore be used as defoliants, desiccants, weedkillers, germination inhibitors and in particular as herbicides. By weed in the broadest sense is meant any plants which grow where they are not wanted. Whether the substances according to the invention act as total or selective herbicides depends essentially on the quantity applied.

The active ingredients according to the invention can be used e.g. with the following plants:

Dicotyledonous weeds of the genera: sinapis, lepidium, galium, stellaria, matricaria, anthemis, galinsoga, chenopodium, urtica, senecio, amaranthus, portulaca, xanthium, convolvulus, ipomoea, polygonum, sesbania, ambrosia, cirsium, carduus, sonchus, solanum, rorippa, rotala, lindernia, lamium, veronica, abutilon, emex, datura, viola, galeopsis, papaver, centaurea.

Monocotyledonous weeds of the genera: echinochloa, setaria, panicum, digitaria, phleum, poa, festuca, eleusine, brachiaria, lolium, bromus, avena, cyperus, sorghum, agropyron, cynodon, monochoria, fimbristylis, sagittaria, eleocharis, scirpus, paspalum, ischaemum, sphenoclea, dactyloctenium, agrostis, alopecurus, apera.

Monocotyledonous crops of the genera: oryza, zea, triticum, hordeum, avena, secale, sorghum, panicum, saccharum, ananas, asparagus, allium.

However, the use of the active ingredients according to the invention is in no way limited to these genera, but also extends in the same manner to other plants.

The compounds are suitable, depending on the concentration, for total weed control e.g. on industrial and track installations and on roads and spaces with and without trees. The compounds can likewise be used for weed control in permanent crops e.g. forests, ornamental trees and shrubs, orchards, vineyards, citrus, nut, banana, coffee, tea, rubber, oil palm and cocoa plantations, berry fruit and hop fields and for selective weed control in annual crops.

The active ingredients according to the invention can be used for weed control as such or in their formulations also mixed with known herbicides, wherein a ready-made formulation or tank mixing is possible.

The active ingredients can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, active ingredient-impregnated natural and synthetic substances and micro-encapsulations in polymeric substances.

These formulations are prepared in a known manner, e.g. by mixing the active ingredients with extenders, thus liquid solvents and/or solid carriers, optionally using surfactants, thus emulsifiers and/or dispersants and/or foaming agents. Where water is used as extender, e.g. organic solvents can also be used as auxiliary solvents. Essentially coming into consideration as liquid solvents are: aromatics, such as xylene, toluene, or alkyl naphthalene, chlorinated aromatics or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, e.g.

petroleum fractions, alcohols, such as butanol or glycol and also their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, and water.

Coming into consideration as solid carriers are:

E.g. natural crushed rocks, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth and synthetic crushed rocks, such as highly dispersed silicic acid, aluminium oxide and silicates; coming into consideration as solid carriers for granules are: e.g. crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite, dolomite and also synthetic granules from inorganic and organic powders and also granules from organic material such as saw dust, coconut shells, corn cobs and tobacco stems; coming into consideration as emulsifiers and/or foaming agents are: e.g. non-ionogenic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, e.g. alkyl aryl polyglycol ethers, alkyl sulphonates, alkyl sulphates, aryl sulphonates and also egg white hydrolysates; coming into consideration as dispersants are: e.g. spent sulphite liquor lignin and methyl cellulose.

Adhesives such as carboxymethyl cellulose, natural and synthetic powdery, granular or latex-like polymers, such as gum arabic, polvinyl alcohol, polyvinyl acetate, can be used in the formulations.

Colourants such as inorganic pigments, e.g. iron oxide, titanium oxide, ferrous cyan blue and organic colourants,

such as alizarin, azole, metal phthalocyanine colourants and micronutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc can be used.

The formulations generally contain between 0.1 and 95 percent by weight of active ingredient, preferably between 0.5 and 90%.

The active ingredients which can be used according the invention can be used for weed control as such or in their formulations also mixed with known herbicides, wherein a ready-made formulation or tank mixing is possible. A mixing with other known active ingredients, such as fungicides, insecticides, acaricides, nematicides, substances for protection against bird damage, growth promoters, plant nutrients and soil structure improvers is also possible.

The active ingredients can be applied as such, in the form of their formulations or in the application forms prepared therefrom by further dilution, such as ready-for-use solutions, suspensions, emulsions, powders, pastes and granules. Application is in the usual manner, e.g. by pouring, spraying, misting, scattering.

The active ingredients according the invention can be applied both before and after the plants have sprouted. The application is preferably carried out before the plants have sprouted, thus in the pre-emergence process. They can also be worked into the ground before sowing.

The quantity of active ingredient used can fluctuate within fairly large limits. It essentially depends on the type of desired effect. In general, the quantities used

are between 0.1 and 50 kg of active ingredient per ha, preferably between 1 and 40 kg/ha.

**Examples of use**

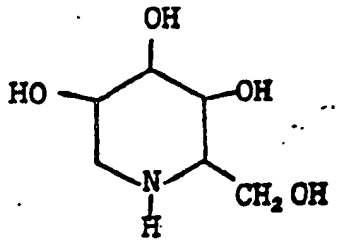
**Pre-emergence test:**

Seeds of lepidium (LEPSA), echinochloa (ECHCG), stellaria (STEME), portulaca (POROL) and poa (POAAN) are laid out in dishes which are filled with vermiculite. A Hoagland's nutrient solution to which the active ingredients according to the invention and the known compound (A) are added in specific quantities is then poured into the dishes. After 2 weeks, the extent of damage to the plants compared with the untreated plants is classified. The classification is as follows:

0% = no effect (as untreated control);
100% = total eradication;
I = inhibition.

Active ingredients, quantities used and results can be seen in table 2 below.

The known compound (A) of the formula:




(A)

2-hydroxymethyl-3,4,5-trihydroxy-piperidine (=1-deoxynojirimycin) serves as comparison.

Table 2

Pre-emergence test / glasshouse

| Active ingredients (cf. preparation examples) | Quantity used kg/ha | % eradicated | | | | |
|---|---|---|---|---|---|---|
| | | lepidium | echinochloa | stellaria | portulaca | poa |
| (A) (known) | 40 | 100 | 0 | 0 | 30/I | 30/I |
| (1) | 40 | 100 | 70 | 40 | 100 | 100 |
| (2) | 40 | 100 | 85 | 80 | 100 | 95 |
| (5) | 40 | 85 | 0 | 20/I | 20/I | 50/I |
| (6) | 40 | 85 | 40/I | 80 | 40/I | 20/I |
| (7) | 40 | 80 | 40/I | 0 | 0 | 80 |

## Result Page



Herbicides agents on basis of Piperidin derivatives

The instant invention concerns the use of to a large extent known 1 - and/or 6-substituierten 2-Hydroxymethyl-3,4,5-trihydroxy-piperidin-Derivaten (=N and/or 1-substituierten 1-Desoxy-nojirimycin derivatives) as herbicides.

It became already known that that pharmacological effective 2-Hydroxymethyl-3,4,5-trihydroxy-piperin (=1-Desoxy-nojfrimycin) of the formula
EMI4.1
(see. DE-OS 26 56 602 also an herbicidal activity exhibits (see. Verff. JP-Ppatentanmeldung No.

55-7224). The 1-Desoxy-nojirimycin is however only a relatively weak herbicide, which in particular does not show satisfactory effect against certain important weeds.

In addition it is known the fact that certain other 3.4.5 - Trihydroxy piperidin derivatives as drug used to become to be able (see. DE-OS 27 58 025; off. EP patent application No. 0,000 947J.Eineherbizide efficacy of these compounds is not however described.

It was now found that the 2-Hydroxymethyl of 3,4, 5 - trihydroxy piperdin derivatives of the general formula
EMI5.1
in which g 1 for alkyl with more than 4 carbon atoms, alkenyl, Alkadienyl, Alkinyl,
Hydroxyalkyl and the grouping - X-R3 stands, whereby X stands for for alkyls or Alkenylen and R for if necessary substituted aryl, if necessary substituted Aryloxy, if necessary substituted Arylmer capto, if necessary substituted
Pyridyl, Alkoxy, Alkoxyalkoxy, alkyl thio, Amino, Hydroxycarbonyl, gege benenfalls substituted Cycloalkyl and if necessary substituted
Cycloalkenyl stands, for g 1 also for hydrogen or alkyl with 1 to 4 carbon atoms stands, if R2 stands for another remainder than hydrogen,
R2 for hydrogen, Cyano, Hydroxy, Hydroxy methyl, Hydroxysulfonyl, Aminomethyl,
Alkylaminomethyl, Hydrqxycarbonyl,
Alkoxycarbonyl as well as the groupings - CO-NH-R4, - CH " - NH-CO-R5, - CH2-NH-SO-R5 - CH2-NH-CO (S) - NH-R5 and - CH2-NH-CO-OR5 stands, how
R4 for hydrogen, alkyl or given if substituted Aralkyl stands, and
5
R for alkyl, if necessary substituted
Aryl, if necessary substituted
Stands for Aralkyl, cyanogen alkyl, aminoalkyl or halo towards alkyl, good herbicides properties exhibit.

The compounds of the formula (I) can be present if necessary as geometric and/or optical isomers.

The instant invention covers both single isomers and the isomeric mixtures.

Surprisingly useful the according to invention 2-Hydroxymethyl-3m4m5-trihydroxy-piperidin-Derivate of the formula (I) shows a significant higher herbicidal activity than the 1-Desoxy-nojirinycin known from the state of the art, which chemical and the effect-moderate nearest compound are. The use according to invention of the fabrics of the formula (I) represents thus an enriching of the technology.

Useful the according to invention 2-Hydroxymethyl-3,4,5trihydroxy-piperidin-Derivate is general defined by the formula (I). In this formula g 1 preferably stands for straight or branched alkyl with 5 to 18 carbon atoms, alkenyl with 2 to 12 carbon atoms, Alkadienyl with 4 to 8 carbon atoms, Alkinyl with 2 to 6 carbon atoms, hydroxyalkyl with 1 to 6 carbon atoms and 1 to 3 hydroxy groups, as well as for the grouping - for X-R3. In addition g 1 also preferably stands for hydrogen or alkyl with 1 to 4 carbon atoms, if R2 stands for another remainder than hydrogen.

X preferably stands for a straight or branched alkylene chain with 1 to 12 carbon atoms or a straight or branched alkenyl chain with 2 to 12 carbon atoms.

R preferably stands for gegenenfalls substituted aryl, Aryloxy and Arylmercapto with in each case 6 to 10 carbon atoms, whereby as substituents preferably mentioned is: Halogen, alkyl with 1 to 4 carbon atoms, halogen alkyl with 1 to 2 carbon and 1 to 5 same or various halogen atoms, Alkoxy, Alkylthio and alkyl sulphonyl with ever 1 to 4 carbon atoms, Hydroxy, Cyano, Nitro, Amino' Alkylamino, Dialkylamino and Alkylcarbonylamino with in each case 1 to 2 carbon atoms for each alkyl radical, Hydroxycarbonyl (- COOH), Alkoxycarbonyl with 1 to 4 carbon atoms in the alkyl radical, as well as if necessary by halogen substituted Phenyl, Phenoxy and benzyle.

R3 stands further preferably for if necessary Pyridyl, for Alkoxy, substituted by halogen and alkyl with 1 to 2 carbon atoms, Alkoxy alkoxy and for Alkylthio with 1 to 4 carbon atoms for each alkyl part, Amino' Hydroxycarbonyl, Alkoxycarbonyl with 1 to 4 carbon atoms in the alkyl part, as well as for if necessary by alkyl with 1 to 4 carbon atoms substituted Cycloalkyl and Cycloalkenyl with in each case 5 to 7 carbon atoms.

▲ top

R2 preferably stands for hydrogen, Cyano, Hydroxy, Hydroxymethyl, Hydroxysulfonyl, Hydroxycarbonyl, Aminomethyl, Alkylaminomethyl with 1 to 4 carbon atoms in the alkyl part, Alkoxycarbonyl with i to 4 Kohlenstofftomen, as well as the groupings - CO-NH-R4, - for CH2-NH-CO-R5, - CH2 NH SO2 R%, - CH2-NH-CO (S) - NH-R5 and - CH2-NH-CO-OR5.

R4 preferably stands for hydrogen, alkyl with 1 to 4 carbon atoms, as well as for if necessary substituted Aralkyl with 6 to 10 carbon atoms in the aryl moiety and 1 to 4 carbon atoms in the alkyl part, whereby as aryl substituents preferably already above the Substitueten inffage mentioned with the definition of the remainder R3 comes.

R5 preferably stands for alkyl with 1 to 12 carbon atoms, cyanogen alkyl and aminoalkyl with 1 to 12 carbon atoms for each for alkyl part, halogen alkyl with 1 to 4 carbon and 1 to 5 same or various halogen atoms, as well as for if necessary substituted aryl and Aralkyl with in each case 6 to 10 carbon atoms in the aryl moiety and 1 to 4 carbon atoms in Alkyl part, whereby as substituents preferably already above the substituents infrage mentioned with the definition of the remainder R3 come.

Bottom halogens is chlorine and fluorine to be understood preferably in each case.

Those active ingredients which can be used according to invention are partial known (see. EP 0,000,947), partly are them subject-matter of own older patent applications (see. the German patent applications P 29 25 943,6 and P 30 07 078,1). The compounds of the formula (I) can become after the there indicated methods prepared. Thus compounds of the formula (I) with R2=OH become obtained, by one in compounds of the formulas (II) or (IIa)
EMI9.1
in those g 1 the indicated above importance has to intercept by careful acid hydrolysis the Isopropylidenoder Cyclohexylidenschutzgruppen remote, whereby it is convenient if necessary, the compounds of the formula (I) with R2 = OH in the form of adducts of the sulfurous acidic ones or prussic acid, formed by ring extension, (R2 = - OS02H or CN). From the Bisulfitadditionsprodukten (i.e. acidic sulfurous acidic esters) the compounds of the formula (I) with R2 = OH become by treatment with bases, preferably alkaline-earth hydroxides like approx. (OH) 2 or Sr (OH) 2, in particular however Ba (OH) 2, in freedom set. By conversion with hydrogen Donor-reducing agents, as for example NaBH4, become from the compounds of the formulas (I) with R-2=OH the compounds of the formula (I) with R2=H recovered.

Certain compounds of the formula (I) can become also obtained, if one the compounds of the formula (I) with R2=OH in actual known manner with prussic acid to compounds of the formula (I) with R =CN converts and if necessary from these by catalytic hydrogenation of the nitrile group compounds with R2= - CH2NH2 manufactures, and the amino group if necessary in actual known manner to compounds, 5 with those R = - CH2-NH-Co-R5 or alkylamine is, acylated, sulfonyliert, alkylated, and/or. with chlorine carbonic acid esters, isocyanates or Senfölen derivati siert.

The compounds of the formula (I), with those R = - COOH is, becomes obtained, by one compounds of the formula (I) with R2= - CN in actual known manner hydrolyzed. From the so obtained carbonic acids compounds of the formula (I) with R2= - COOAlkyl by conversion with corresponding alcohols, compounds of the formula (I) with R2= - leave themselves to CONHR4 by Aminolyse of the esters with amines 4 of the general formula R - NH2 obtained in actual known manner.

N-substituted compounds of the formula (I) with R2=H become also obtained, if one the compound of the formula (III), i.e. 1-Desoxy-nojirimycin,
EMI11.1
either with aldehydes of the formula
O = CH - g 1 (IV) in which
G 1 the indicated above importance has, in presence of a hydrogen Donor-reducing agent converts, or with reactive alkylating agents of the formula Z-R1 (V) in which
G 1 the indicated above importance has and
Z for halogen or - OSO3-Gruppe is located, in conventional manner converts. In place of the compounds of the formula (V) also different reactive alkylating agents can, like e.g. Ethylene oxide, used become.

Other details to the various. Procedures know that off. EP-patent application No.

0,000,947 as well as the subsequent manufacture with plays removed becomes.

The starting products of the formulas (II), (), (III), (IV) and (V) are general known compounds of the organic chemistry, and/or. they and their preparation are in the EP-patent application No. 0,000,947 described.

Production examples: Example 1
EMI13.1
90.0 g 1-Desoxynojirisycin (A) became in 450 ml H2O dissolved and saturated with 50C with CO2. The mixture became 20 hours with 200C agitated, then and again with CO2 saturated cooled on 5 " C. 27.97 g ethylene oxide became liquid weighed and added in a casting.

The reaction mixture became 30 minutes with 50C to 100C agitated, then and 6 hours heated within 30 minutes on 500C with 50 C agitated. After other 20-hour agitation with 200C one regenerated. The reaction mixture became at the rotary evaporator concentrated, the residue became with 2-Methoxyethanol simmering heated and with Setivkohle clarified. One let the product crystallize with 200C. It was washed afterwards aspirated, with 2-Methoxyethanol, then with ethanol and dried. The so obtained 84.2 g n (ss-Hydroxyethyl) - 1-desoxynojirimycin with a melting point of 144-145,50C were recrystallized from 90%igem ethanol. Yield at n (ss-Hydroxy ethyl) - 1-desoxynojirimycin (1) 78.3 g with a melting point of 147-1490C.

The compound (1) can do also as 1 (B-Hydroxyethyl) - 2 - hydroxymethyl-3,4,5-trihydroxy-piperidin referred become.

Preparation of the starting product
EMI14.1
A solution of 2 g 5-Amino-5-desoxy-1,2-isopropyliden a-D-glucofuranose in 8 ml 2 n hydrochloric acid becomes 24 hours agitated. It is verdSinnt with 5 ml waters and after addition of 0,69 g triethylamine and 0.3 g Raney nickel 5 hours at 3,5 bar of hydrogenated. It becomes concentrated concentrated in the vacuo of the catalyst filtered and still twice in each case after addition of little ethanol, whereby crystallization occurs. The crystals are mixed with ethanol, aspirated and good with ethanol washed. One receives 1-Desoxxy-nojirimycinhydrochlorid (A) from the melting point 209-2100C bottom decomposition to 1.45 g (79.7% of the theory).

From the hydrochloride the free base becomes obtained in conventional manner.

Example 2
▲ top
EMI15.1
To 7.4 g 1-Desoxynojirimycin in 150 ml to methanol and 6.7 ml glacial acetic acid gives one 17 ml 10-Undecenol and 3 g sodium

cyanogen boron hydride (NaCNBH3). One agitates 2 hours with room temperature. Subsequent one becomes the reaction mixture on one with strrk acidic ion exchanger (H@-Form) filled column aufgeteagen. It becomes first with methanol/Wasser=2: 1, subsequent with ethanol/6%-igem Ammoniak=2: 1 eliminated. The ammoniakalische eluate becomes concentrated. The residue becomes from water crystallized. Yield: 11.7 g N-Undecen-10-yl1-dexoxy-nojirimycin (2) of the melting point 144-1460C.

Example 3
EMI15.2
To 200 ml waters and 21.2 g Ba (OH) one gives 17.5 g Nojirimycinbisulfitaddukt to 2 x H2O. One agitates an hour with room temperature and sucks the solid off.

The filtrate staggered one prussic acid liquid with 12 ml and lets 1/2 hour agitate. The solution becomes again filtered and at the rotary evaporator up to 20 ml concentrated. One staggered first with 20 ml methanol, whereby the desired product begins to crystallize, and the completed crystallization by addition of 100 ml ethanol. The precipitation becomes aspirated.

Yield: 12.0 g 1-Cyano-1-desoxynojirimycin (3) of the melting point 152-1530C. After recrystallization from methanol and little water the substance melts with 155-1560C.

Example 4
EMI16.1
5 g l-Cyano-l-desoxynojirimycin (example 3) become into 100 ml waters with 10 g Raney nickels as catalyst an hour with 3,5 atmospheres H2-Druck in a vibration pear hydrogenated. Then will of the catalyst aspirated and the solution becomes at the rotary evaporator to dry brought. The residue will in little simmering methanol received, the solution again becomes filtered and dry brought. The residue becomes out approx. 15 ml methanol recrystallizes.

Yield: 3.4 g 1-Aminomethyl-1-desoxynojirimycin (4) of the melting point 148-1500C. After renewed crystallization from methanol the melting point rises to 154-1550C.

Example 5
EMI17.1
To 6.42 g 1-Aminomethyl-1-desoxynojirimycin in 100 ml methanol and 20 ml waters drips one with -75 C 5.06 ml 6-Isocyanatohexansäurenitril too. It becomes an half hour with -75 C agitated. Then one lets slow warm up to room temperature (3 hours). The reaction solution becomes concentrated and the residue from methanol crystallized.

Yield: 4.8 g 1 (N'-5-Cyano-pentylureidomethyl) - 1desoxynojirimycin (5) of the melting point 160-165 C.

Example 6
EMI17.2
The preparation made in analogy to example 2.

Melting point: 162 C Example 7
EMI18.1
To 0.8 mol Desoxynojirimycin and 1.12 mol potassium carbonate in 1,3 one gives 1 dimethylformamide bottom agitations with room temperature 1.12 mol Sorbylbromid. The temperature rises to 400C. One lets 2.5 hours after-agitate with room temperature, sucks the failed salts, takes up the filtrate in 2000 ml to waters off and extracted it twice with ever 500 ml ethers. The Dimethyl form amide/water phase is mixed in the vacuo concentrated, the residue with 1,4 1 acetone and the failed solid aspirated. This will become then with 1,5 1 ethanol expenditure-cooked and the residual salts filtered. The final product crystallized out, is recrystallized aspirated and from water (14 ml waters on 10 g product). One receives -1 - desoxynojirimycin (7) from the melting point 172-1730C in 30%-iger yield n (Hexa-2, 4-dienyl).

In analogous manner and the corresponding indicated procedure ways the compounds of the formula (I) of the subsequent table become 1 obtained: Table 1
EMI19.1

EMI19.2

<tb>
<tb> <September> Physical one
<tb> <September> COMPUTER CENTRE <SEPTEMBER> R2 <September> Constant one
<tb> 8 <September> H <SEPTEMBER> Fp: 111-13 <September> Degrees
<tb> 8 <September> - CH2 (CH2) 5-CH3 <September> H <SEPTEMBER> Fp: <September> 13 C
<tb> 9 <September> - CH2 <SEPTEMBER> to <September> H <SEPTEMBER> Fp: 183-640C
<tb> 10 <September> - CH2 <SEPTEMBER> < <September> H <SEPTEMBER> Fp: 174-750C
<tb> 11 <September> - CH2-CH (OH) - CH2OH <SEPTEMBER> H <SEPTEMBER> m/e=206,176
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<tb> 13 <September> - cH2-COOH <September> H <SEPTEMBER> Fp: 187-880C
<tb> 14 <September> Q2N <SEPTEMBER> D <SEPTEMBER> H <SEPTEMBER> Rf-Wert=0,85
<tb> 15 <September> - CH2 <SEPTEMBER> g <September> H <SEPTEMBER> Rf-Wert=0,7*
<tb> <September> HOOC
<tb> 16 <September> CH2 <SEPTEMBER> zuCOOH <September> H <SEPTEMBER> Fp: 280-810C
<tb> 17 <September> - CH2-CH2 <SEPTEMBER> e <September> H <SEPTEMBER> Fp: 179-810C
<tb> 18 <September> - (CH2) 5-cH <September> H <SEPTEMBER> Fp: 112-130C
<tb> 19 <September> - (C) 7-cH3 <September> H <SEPTEMBER> Fp: 115-170C
<tb> 20 <September> - (CH; <September> ) 8 <September> - CHs <September> H <SEPTEMBER> Fp: 105-070C
<tb>
EMI20.1

<tb> Bsp <September> . <September> G 1 <September> R2 <September> Physical one
<tb> NR <September> . <September> Konstarlte
<tb> 21 <September> - <September> ( <September> CH2 <SEPTEMBER> ) <September> 9 <September> - CH3
<SEPTEMBER> H <SEPTEMBER> Fp: <September> 151 <September> C
<tb> 22 <September> - <September> (CH2 <SEPTEMBER> ) 11-CH3 <September> H <SEPTEMBER> Fp: 1640C
▲ top <tb> 23 <September> - (CH2 <SEPTEMBER> ), 3-CH3 <September> H <SEPTEMBER> Fp: 105-070C

<tb> 24 <September> - (cH2) 4-CH29H <September> H <SEPTEMBER> Fp: 86-870C
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<tb> 26 <September> cHa <September> t <September> H <SEPTEMBER> Fp: 142-440C
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<tb> 28 <September> KHz <September> C <SEPTEMBER> O) - C <SEPTEMBER> H <SEPTEMBER> Fp <September> : 153-55 <September> " <September> C
<tb> 29 <September> - CH, <SEPTEMBER> IO) <September> H <SEPTEMBER> Fp: 134-36 C
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<tb> 32 <September> - CH2-CH=C1I2 <SEPTEMBER> H <SEPTEMBER> Fp: 131-320C
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<tb> 34 <September> CHa <September> vC1 <September> H <SEPTEMBER> Fp <September> H <SEPTEMBER> : 130-32 C
<tb> 35 <September> - CH2 <SEPTEMBER> tNo2 <September> H <SEPTEMBER> Fp: 144-460C
<tb> 36 <September> - CH, <SEPTEMBER> - <September> H <SEPTEMBER> Fp: 168-700C
<tb> 37 <September> cH3 <September> - CN <SEPTEMBER> m/e: 171,157,144
<tb> 38 <September> H <SEPTEMBER> - COOH <SEPTEMBER> Fp: 267-700C
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<tb> 40 <September> - <September> - COOC2 <SEPTEMBER> H5 <September> m/e=218,200,176
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EMI21.1

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<tb> 47 <September> - CH3 <SEPTEMBER> - CH2-NH-CO <SEPTEMBER> p: 135-360C
<tb> 48 <September> H <SEPTEMBER> - CH2-NH-SO2 <SEPTEMBER> O <SEPTEMBER> - CH3 <SEPTEMBER> Fp: 173-75 C
<tb> 49 <September> cH3 <September> - CHNH-SQ-OO-CH3Fp: 218-19oC
<tb> 50 <September> H <SEPTEMBER> - CH2-NH-CO-NH <SEPTEMBER> O <SEPTEMBER> Fp: 161-620c
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<tb> 53 <September> - CH2CH2-SCH3 <SEPTEMBER> H <SEPTEMBER> m/e:: 220,206,176
<tb> 54 <September> - CH2CH2-SC2H5 <SEPTEMBER> H
<tb> 55 <September> - CH2 <SEPTEMBER> OH2 <SEPTEMBER> OCH2 <SEPTEMBER> OH2 <SEPTEMBER> STILL,
<tb> 56 <September> - (CH2) <SEPTEMBER> ) 8-cH3 <September> - CH2 <SEPTEMBER> - NH-COCH3 <SEPTEMBER> mXe: 329,288
<tb> *
<tb> 57 <September> H <SEPTEMBER> - CH2-NH (CH2 <SEPTEMBER> ) 8 <September> Rf-value: 0,52*
<tb> <September> CH3
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<tb> 59 <September> - (KHz) 5-O <September> H <SEPTEMBER> Fp: 138-39 C
<tb> 60 <September> - (CH2) *CO <SEPTEMBER> O <SEPTEMBER> H <SEPTEMBER> Fp: 1100C
<tb> 61 <September> CH3 <SEPTEMBER> ) <September> H <SEPTEMBER> Fp: 155-56 C
<tb> CH,
<tb> <September> CH3
<tb> 62 <September> - CH2CH2CH2-O <SEPTEMBER> W <SEPTEMBER> H <SEPTEMBER> Fp: 128 C
<tb> <September> EAR
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<tb> 63 <September> - CH2CH2-O <SEPTEMBER> -0-0-01 <September> H <SEPTEMBER> Fp: 175-76 C
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<tb> 65 <September> - CH2-CH=CH-CH2-o <September> to <September> H <SEPTEMBER> Fp: 1200C (xH, O)
<tb> 66 <September> - CH2-CH=CH-CH2-O <SEPTEMBER> -0-GO <September> - OH3 <SEPTEMBER> H <SEPTEMBER> Fp: : 163-66 C
<tb> 67 <September> - CH, <SEPTEMBER> - CH-CH-CH, <SEPTEMBER> -9 <September> H <SEPTEMBER> H <SEPTEMBER> Resin
<tb> <September> OOC2H5
<tb>
EMI22.1

<tb> Ex. <September> G 1 <September> R2 <September> Physical one
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<tb> 69 <September> OH2 <SEPTEMBER> OH2 <SEPTEMBER> -0-Go <September> -01 <September> H <SEPTEMBER> Fp: 156-57 C
<tb> 70 <September> -0H20H2-0-QO-CN <September> H <SEPTEMBER> Fp: 125 C
<tb> 71 <September> - CH2CH2-O <SEPTEMBER> H <SEPTEMBER> H <SEPTEMBER> Fp: 132-340C
<tb> 72 <September> - CH2CH2-S <SEPTEMBER> H <SEPTEMBER> H <SEPTEMBER> Fp: 121-230C
<tb> 73 <September> - CH2CHz-S <September> - s (n7 <September> - CH3 <SEPTEMBER> H <SEPTEMBER> ~ <September> Fp: 126-27 C
<tb> <September> OH3
<tb> 74 <September> - CH2-CH=CH-CH2-S <SEPTEMBER> H <SEPTEMBER> Fp: 106C
▲ top <tb> 75 <September> - CH2-CH=qH-OH2-SO1 <September> H <SEPTEMBER> Fp: 93-9T " C

<tb> 76 <September> - CH2-CH=CH-CH2-- <September> H <SEPTEMBER> Fp <September> :: 138-40 <September> 0 <September> C
<tb> <September> I
<tb> <September> CtCH3) 3
<tb> 77 <September> - CH, <SEPTEMBER> - CH=CH-CH, <SEPTEMBER> -9 <September> H <SEPTEMBER> Fp: <September> 2830C
<tb> <September> X
<tb> <September> tH3
<tb> 78 <September> - CH2-CH=CH-CH2-O <SEPTEMBER> O < <September> H <SEPTEMBER> Fp: 165-69 C
<tb> 79 <September> - CH2 (CH=CH) 2-C2H5 <September> H <SEPTEMBER> Fp: 135-37 C
<tb> 80 <September> - CH2-CH=CH-CH3 <SEPTEMBER> H <SEPTEMBER> Fp: 120-23 C
<tb> 81 <September> - CH2-CH=CH <SEPTEMBER> H <SEPTEMBER> Fp: 112-18 C
<tb> <September> C (CH3 <SEPTEMBER> ) 2-0H2
<tb> <September> C~Hg t
<tb> * Rf-values certain on DC finished plates of the company
Merck, silica gel 60; Flow material: Ethyl acetate/Metha nol/H20/25% ige wässr. Ammonia = 100/60/40/2 (volume parts). - To. Comparison: Rf-value. of 1-Des oxynojirimycin (A) - = 0.3.

The active ingredients according to invention affect the Po one zenwachstum and can therefore as Defoliants, Desiccants, herb killing means, germ inhibition means and as weed killer used become in particular. Bottom weeds in the broadest sense all plants are to be understood, which grow up at loci, where they are undesirable. Whether the fabrics according to invention work as total or selective herbicides, essentially depends on the applied amount.

The active ingredients according to invention can e.g. with the subsequent plants used become: Dikotyle of weeds of the genera: Sinapis, Lepidium, Galium, Stellaria, Matricaria, Anthemis, Galinsoga, Chenopodium, Urtica, Senecio, Amaranthus, Portulaca, Xanthium, Oonvolvulus, Ipomoea, Polygonum, Sesbania, Ambrosia, Cirsium, Carduus, Sonchus, Solanum, Rorippa, Rotala, Lindernia, Lamium, Veronica, Abutilon, Emex, Datura, Viola, Galeopsis, Centaurea.

Monokotyle of weeds of the genera: Echinochloa, Setaria, Panicum, Digitaria, Phleum, Poa, Festuca, Eleusine, Brachiaria, Lolium, Bromus, Avena, Cyperus, sorghum, Agropyron, Cynodon, Monochoria, Fimbristylis, Sagittaria, Eleccharis, Scirpus, Paspalum, Ischaemum, Sphenoclea, Dactyloctenium, Agrostis, Alopecurus, Apera.

Monokotyle cultures of the genera: Oryza, Zea, Triticum, Hordeum, Avena, Secale, sorghum, Panicum, Saccharum, pineapple, Asparagus, Allium.

The use of the active ingredients according to invention is however by no means on these genera limited, but extended in same way also on other Po one zen themselves.

The compounds are e.g. suitable in dependence of the Kon zentration for the total weed control. on Industrieund railway tracks and at pathways and places with and without tree vegetation. Just as the compounds can for weed control in continuous cultures e.g. Forest, ornamental shrub, fruit, manner, Citrus--, Nut, banana, coffee, dte, rubber, blpalm, cocoa, potato berry and hop plants and for selective weed control in one year's Kul doors used become.

The active ingredients according to invention can find as such or in their formulations also in mixture with known herbicides for weed control use, whereby formulation of finished or tank mixture is possible.

The active ingredients can become into the conventional formulations converted, like solutions, emulsions, suspensions, powder, foams, pastes, granulates, active ingredient iEprägnierte nature and synthetic fabrics and purifying encapsulations in polymere fabrics.

These formulations become in known manner herge place, e.g. by mixing the active ingredients with putting means, thus liquid solvents and/or solid inertial materials, if necessary using surface-active agents, thus emulsifying agents and/or dispersing agents and/or foam-producing agents.

In case of the use of water as extenders can e.g. also organic solvents as auxiliary solvent used become. As liquid solvents essentially come into question: Aromatics, like xylene, toluene, or alkyl naphtha LINE, chlorinated aromatics or chlorinated aliphatic hydrocarbons, like chlorobenzenes, Chlorethylene or methylene chloride, aliphatic hydrocarbons, like cyclohexane or paraffins, e.g. Petroleum fractions, alcohols, like Butanol or glycol as well as their ether and ester, Ketone, like acetone, methyl ethyl ketone, methyl isobutyl ketone or Cyclohexanon, strong polar solvents, like dimethylformamides and dimethylsulfoxide, as well as water.

As solid inertial materials come into question: Z. - B. natural powdered minerals, like Kaoline, aluminas, talcum powder, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth and synthetic powdered minerals, like high-disperse silicic acid, alumina and silicates; as solid inertial materials for granulates come into question: e.g.

broken and fractional natural rocks such as Calcit, marble, pumice, sepiolite, dolomite as well as synthetic granulates from inorganic and organic flours as well as granulates from organic material such as saw flour, coconut bowls, ear of corn and tobacco stack; as emulsify and/or foam-producing agents come into question: e.g. nichtionogene and anionic emulsifiers, like Polyoxyethylen fatty acidester, Polyoxyethylen fatty alcoholether, e.g. Alkylarylpolyglykol ether, alkyl sulfonates, Alkylsuifate, Arylsulfonate as well as EiweiShydrolysate; as dispersing agents come into question: e.g. Lignin Sulfitablaugen and methyl cellulose.

Adhesives can become such as carboxymethyl cellulose, natural and synthetic powdery, granular or latexförmige polymers used, like Gummiarabicum, Polvinylalkohol, polyvinyl acetate in the formulations.

Dyes can do such as inorganic pigments, e.g.

Iron oxide, titanium oxide, ferrous cyan blue and organic dyes, like alizarine, Azol, Metallphthalocyaninfarbstoffe and Spurennälirstoffe such as salts of irons, manganese, boron, copper, cobalt, molybdenum and zinc used become.

The formulations contain generally between 0,1 and 95 weight percentage active ingredient, preferably zwischan 0.5 and 90%.

Useful the according to invention active ingredients can find as such or in their formulations also in mixture with known herbicides to the Unkraubekämpfung use, whereby formulation of finished or tank mixture is possible. Also a mixture with other known active ingredients, like fungicidal one, insecticides, Akariziden, Nematiziden, protective agents bird-ate approximately, from stature materials, plant nutrients and soil structure improvement averages is possible.

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The active ingredients can become as such, in form of their formulations or the embodiments, like ready for use solutions, prepared from it by other diluting, suspensions, emulsions, powders, pastes and granulates applied. The application happens in conventional manner, e.g. by pouring, syringes, spraying, litters.

The active ingredients according to invention can become both before and after accumulating the plants applied.

The application becomes preferably made before accumulating the plants, thus in the pre emergence method.

They can become also before the seed into the soil incorporated.

The spent active substance quantity can vary in larger ranges. It essentially depends on the type of the qewtlnschten effect. Generally the application rates lie between 0,1 and 5G kg active ingredient per hectar, preferably between 1 and 40 kg/ha.

Use examples Pre emergence test: In dishes, which are with vermiculites filled, seeds become. of Lepidium (LEPSA), Echinochloa (ECHCG), Stellaria (STEME), Portulaca (POROL) and Poa (POAAN) construed. The dishes. become then with a Hoagland broth poured, that the active ingredients according to invention and the known compound (A) in certain amounts added. are. After 2 weeks the damage degree of the plants Xt comparison is bonitiert to the untreated plants. Mean: O % = no effect (like untreated control);
100% 3 total destruction, H = inhibition.

Active ingredients, application rates and results come out from the subsequent table 2.

As comparison means the known compound serves (A) of the formula:
EMI28.1
2-Hydroxymethyl-3,4,5-trihydroxy-piperidin (=1-Desoxynojirimycin). Table 2 Pre emergence test/greenhouse of active ingredients effort % killing (see. Herstel mixes Lepidium Echinochloe Stellaria Portulaca Poa lungsbeispiele) kg/ha (A) 40,100 0 0 30/H 30/H (1) 40,100 70 40 100,100 (2) 40,100 85 80 100 95 (5) 40 85 0 20/H 20/H 50/H (6) 40 85 40/H 80 40/H 20/H (7) 40 80 40/H 0 0 80

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